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THE

PHYSICAL REVIEW

OBSERVATIONS ON THE STARK EFFECT IN HYDROGEN AND HELIUM

By J. Stuart Foster

Abstract

Stark effect measurements for hydrogen and helium lines in fields 1 to 38 kv/cm.—The *Lo Surdo method was improved* by using a rotating cathode to minimize pitting. A three prism glass spectrograph, and a Hilger quartz spectrograph E_1 were used. Enlargements of the spectrograms for Hγ and for six He lines are given. (1) *Hydrogen Balmer lines.* At fields below 3 kv/cm, the red side of each line is more diffuse than the violet side, in agreement with Kramers' theory of the connection between the Stark effect components and the fine structure components. For fields above 5 kv/cm ten p components of Hγ are symmetrically arranged, the ratios of $\Delta\lambda$ to field coming out $\pm$(.230, .191, .153, .065, .026) A/kv/cm. Changes in the relative intensities of components of Hγ and of Hδ with increasing field are noted and the observed relative intensities of Hϵ are found to agree fairly well with Kramers' theoretical predictions. (2) *Parhelium lines.* Measurements at five field strengths are given for the groups near the D lines 4388, 4144, 4009, and near λ3614, including some new components. The number of lines in each group increases with the order. Combination series of the type $2P-mQ$, $2S-mQ$ ($Q=S, P, B, E, F, \ldots$; $M=4, 5, 6 \ldots$) are suggested which include these lines and also the components of Stark's "diffuse principal" series and which fit into the scheme proposed by Tschulanowsky. The variable behavior of lines near λ4388 in low fields is noted and observations are given for the λ3927 group. As a rule the *Stark effect pattern* is constant for the members of each series but varies with the series. Many components vanish with increasing field. (3) *Orthohelium lines.* Measurements are given for groups λ3820 and λ3705 and observations for λ4026.

Introduction

THE effect of high electric fields on the lines of the Balmer series has been observed by Stark[1] and is well known. The explanation is based on the quantum theory and was given independently by Epstein[2] and Schwarzschild.[3] Kramers[4] has used the principle of correspondence

[1] J. Stark, Ann. der Phys. **48**, 193 (1915)
[2] P. Epstein, Ann. der Phys. **50**, 489 (1916)
[3] K. Schwarzschild, Ber. Akad. Berlin, p. 548, 1916
[4] H. A. Kramers, Det. Kgl. Danske Vidensk. Skrifter, Naturo. og Math. Afd., 8 Raekke, III. 3 (1919)

to explain the polarizations and relative intensities of the components observed in hydrogen and ionized[5] helium. We are indebted to the same author for an account of the behavior of new fine structure components of the Balmer series in very weak fields. In a later paper Kramers[6] has discussed the gradual change from the fine structure to the commonly observed Stark effect, and has represented the detailed connections for Hα and He λ4686. From this important paper one may conclude that the Stark effect pattern contributed by a fine structure line varies with the type of the line.

The Stark effects to be expected in the case of the fine structure lines in the Balmer series are as follows.

Transition associated with emission of fine structure component	Stark effect components contributed by fine structure component	
	Parallel	Perpendicular
n_1-2_1	1	0
n_k-2_1 ($k=2, 3, 4$, etc.)	1	1
n_1-2_2	1	1
n_2-2_2	2	2
n_k-2_2 ($k=3, 4, 5$, etc.)	2	3

In any Balmer line the group of fine structure components corresponding to transitions to the 2_1 orbit contribute a Stark effect group pattern of imperfect symmetry in which the components do not intersect one another. A somewhat similar though greater contribution to the group pattern in the electric field is made by the fine structure components emitted when the electron passes to the 2_2 orbit. These two groups of fine structure components of a single Balmer line are so close together that many Stark effect components from one group cross components from the other group. The structure at very low fields is thus considered to be very complicated and quite beyond complete experimental inquiry.

This view of the connections between the fine structure and the Stark effect components in hydrogen at once suggests an interpretation of the effect of an electric field on the spectra of heavier atoms. Bohr[7] has called attention to some "isolated components" observed by Nyquist near the diffuse lines of both systems in neutral helium. These he believes to be new combination lines corresponding to transitions which cannot occur in the absence of the field. He observes that in addition to lines in the Koch[8] series $2p-mp$ and the corresponding parhelium series

[5] H. Nyquist, Phys. Rev., **10,** 226 (1917); also J. Stark, O. Hardtke and G. Liebert, Ann. der Phys. **56,** 569 (1918)

[6] Kramers, Zeit. f. Phys. **3,** 199 (1920)

[7] N. Bohr, The Quantum Theory of Line Spectra, Part III.

[8] J. Koch, Ann. der Phys. **48,** 98 (1915)

$2P-mP$, Nyquist's data include new lines which fit the formulas $2p-mb$ and $2P-mB$, $(m=4,5)$.

Quite recently Tschulanowsky[9] has measured certain lines on plates taken by Paschen during the examination of the fine structure of Fowler's series in ionized helium. These are believed to be members of the neutral helium series $2p_{1,2}-mb$ (measured for $m=4,5$) and $2P-mB$ (measured for $m=4,5,6,7$). The measurements indicate that the electric field in the source was very weak.

Tschulanowsky gives a sketch of line series which, by analogy with hydrogen, might appear in the systems of neutral helium. These are limited to those emitted when the electron passes to orbits with principal quantum number 2. They are

Parhelium	Orthohelium
$2S-mQ$	$2s-mq$
$2P-mQ$	$2p-mq$

where $Q=S,P,D,B,E,F,G$, etc., and $q=s,p,d,b,e,f,g$, etc. B refers to Bergmann terms; E,F,G to terms associated with orbits which have azimuthal quantum numbers 5,6,7 respectively. It is suggested that the lines of Stark's" diffuse principal" series in both systems are represented in the electric field by a single parallel component and a single perpendicular component, and that the other "components" reported are in reality new combination lines not attached to the diffuse lines at "zero" field.

The classification of the neutral helium spectra just presented was also suggested by the author.[10] The suggestion was based on the experimental evidence given in the present paper. It is found that the study of the Stark effect often assists in the identification of a combination line.

Method

The method is a modification of that first used by Lo Surdo. A vertical cross-section of the central portion of the discharge tube is shown in Fig. 1. The light to be examined passes out through the slit S. In order to prevent pitting of the cathode by the action of the positive ions and the consequent change in the electric field near it, the cathode is arranged so that it can be frequently turned about the axis of the tube, exposing new surface.

In the experiments here reported, a 4 kw motor-generator supplied a 500 cycle current to the primary of a standard 110-13200 volt trans-

[9] W. Tschulanowsky, Zeit. f. Phys. **16,** 300 (1923)

[10] J. S. Foster, Proc. Am. Phys. Soc. Phys. Rev. **23,** 293 (1924). When this note was written the author was unaware of the earlier interpretation by Professor Bohr.

former designed for 60 cycles. The secondary current was rectified in the usual manner, and the ripples were reduced to a very low value by sufficient capacity and inductance. The voltage on the tube (5 to 8 kv) was kept constant by the adjustment of a resistance in the primary of the transformer.

The vacuum system contained a ballast capacity of 16 liters. Hydrogen and helium were mixed in various proportions. The hydrogen increased the light intensity; moreover it was convenient to have the Balmer lines on the plates. The current was 5 m-amp. to 20 m-amp.

Immediately in front of the discharge tube was a double-image prism. The images were focused on the slit by a rapid rectilinear lens of 50 cm focal length. The tube support, double-image prism, lens, and spectro-

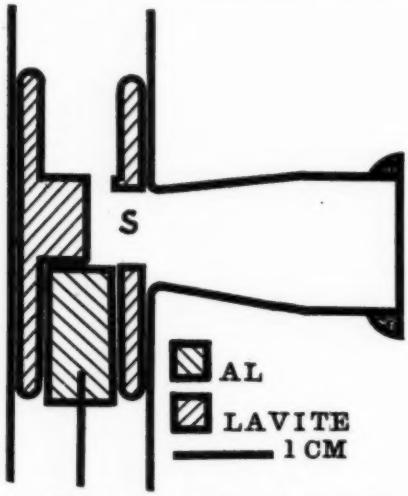

Fig. 1. Modified Lo Surdo tube with rotating cathode.

graph were so connected as to form a very rigid system. Two spectrographs were employed. Fig. 2 is taken from a plate exposed for 50 minutes in a newly mounted glass prism spectrograph, with six prisms of which only three have been used. The dispersion is 6 A/mm at $H\gamma$. The mountings are of metal throughout. This instrument, which contains a few new features, is described in the J. Op. Soc. Am., 8, 373, 1924. Fig. 3 is from a plate exposed 1.5 hr in a Hilger quartz spectrograph, type E_1. The arrows indicate new lines.

Results for Hydrogen Balmer Lines

By means of a canal-ray tube, Stark and Kirschbaum[11] found that in strong electric fields each line of the Balmer series was replaced by a

[11] J. Stark and H. Kirschbaum, Ann. der Phys. **43**, 991 (1914)

symmetrical group of lines each one of which was displaced from the position of the original line by an amount proportional to the field. This fundamental research has enabled later investigators to determine field strengths from separations of conveniently chosen components in

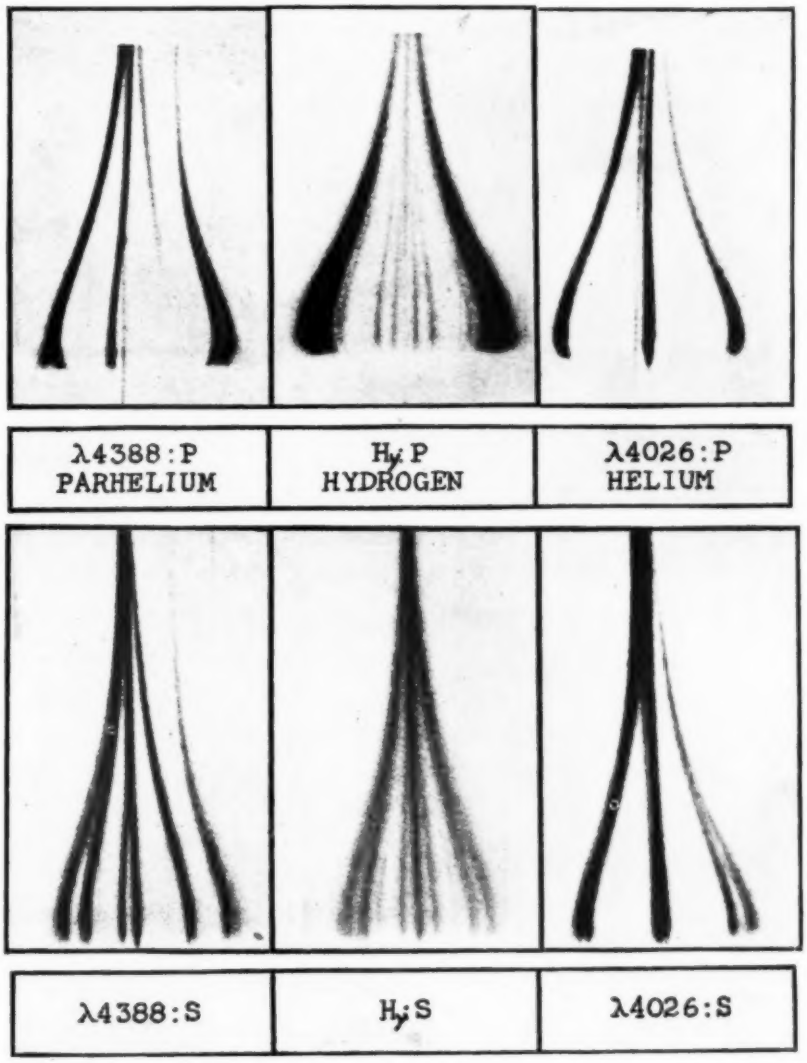

Fig. 2. From a plate taken with glass prism spectrograph. Magnification × 8.

some Balmer pattern. Moreover, since the Stark effect for each Balmer line is well known, any such line may be used as a guide by which to judge the quality of the analysis obtained by Lo Surdo's method for

other lines on the same plate. Because of its photographically convenient wave-length and moderate intensity, Hγ has been employed for this double purpose. Although the Stark effect for this line is well known at high fields, a few details have been observed at lower fields which seem to be of sufficient interest to record. To these are added a few notes on Hε and on the general behavior of the Balmer lines in very low fields.

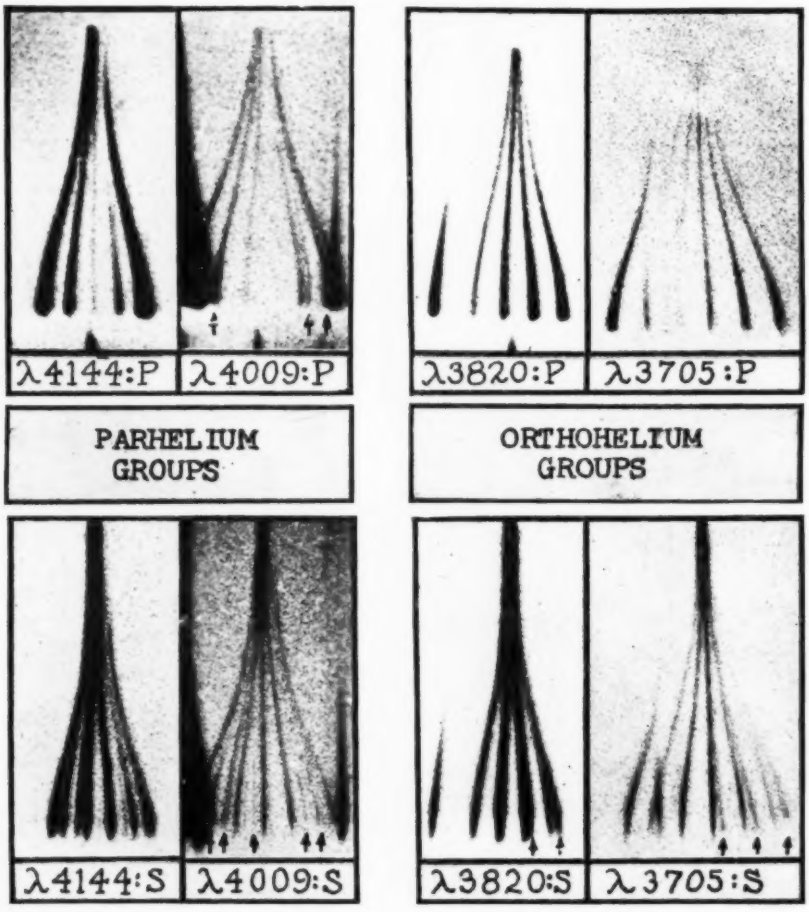

Fig. 3. From a plate taken with quartz spectrograph. Magnification × 8.

Fine analysis of Hγ. The fine analysis for the parallel components of Hγ is given in Table I for ten field strengths ranging from 4.6 kv/cm to 38.0 kv/cm. The perpendicular components have not been measured in a similar way because of their slightly inferior quality. This defect was brought about by the fact that the two images formed by the

Rochon prism did not focus in the plane of the slit. It is assumed that the separation of the strong outer parallel components may be used to determine the field strengths. On this basis, and through the use of Stark's[12] most recent data, the measurements are plotted in Fig. 4. All components are found to have displacements very nearly proportional to the field, for the range of fields here considered, the ratios being $\pm$(.230, .191, .153, .065, .026)A/kv/cm. As Stark[13] has reported a considerable asymmetry in his rough analysis at 28.5 kv/cm, it should be noted that the symmetry is disturbed very little.

TABLE I

Parallel components of Hγ

Field	Δλ from strongest fine structure comp. in zero field	
38.0 kv/cm	8.78 7.26 5.80 2.52 1.02	8.75 7.30 5.80 2.47 1.02
34.7	7.99 6.59 5.34 2.27 0.90	7.94 6.60 5.35 2.22 0.91
28.9	6.68 5.55 4.51 1.90 0.81	6.60 5.55 1.86 0.75
23.3	5.39 4.49 1.53 0.66	5.30 4.38 1.43 0.54
18.4	4.24 3.58 1.20	4.21 3.57 1.20
14.2	3.30 2.78	3.24 2.81
10.6	2.44	2.43
7.9	1.77	1.88
5.8	1.26	1.39
4.6		1.08 0.90

The displacements just recorded are measured from an undisplaced line. This line was produced by a comparatively faint glow in the side tube leading from the main discharge. It is very sharp and probably represents no more than the strongest component in the fine structure of Hγ.

Changes in relative intensities of components of Balmer lines with increasing field. (a) In moderate fields the components on the red side of each original line are usually stronger than the corresponding ones on the violet side. This is true of all lines observed, Hβ to Hε inclusive, and is an effect observed by Stark in a canal-ray tube when the canal-rays were accelerated by the electric field. In a field of 104 kv/cm, however, Stark found perfect symmetry. (b) The parallel components $5_0-2_{\pm 1}$ (Kramers' notation) for Hγ are weaker than $5_{\pm 1}-2_0$ when they first appear on the plate; but in the highest fields they are the stronger, just as observed by Stark. (c) In low fields the first of the weak outside perpendicular components of Hγ to appear is 5_4-2_0 and this is the one which, on the theory, has its origin in a fine structure line present at zero field. Its intensity increases very little with increasing field. On my plates there is no evidence of the components $5_{\pm 3}-2_{\mp 1}$ although

[12] J. Stark, Ann. der Phys. **48**, 193 (1915)

[13] Stark, Monograph, p. 51

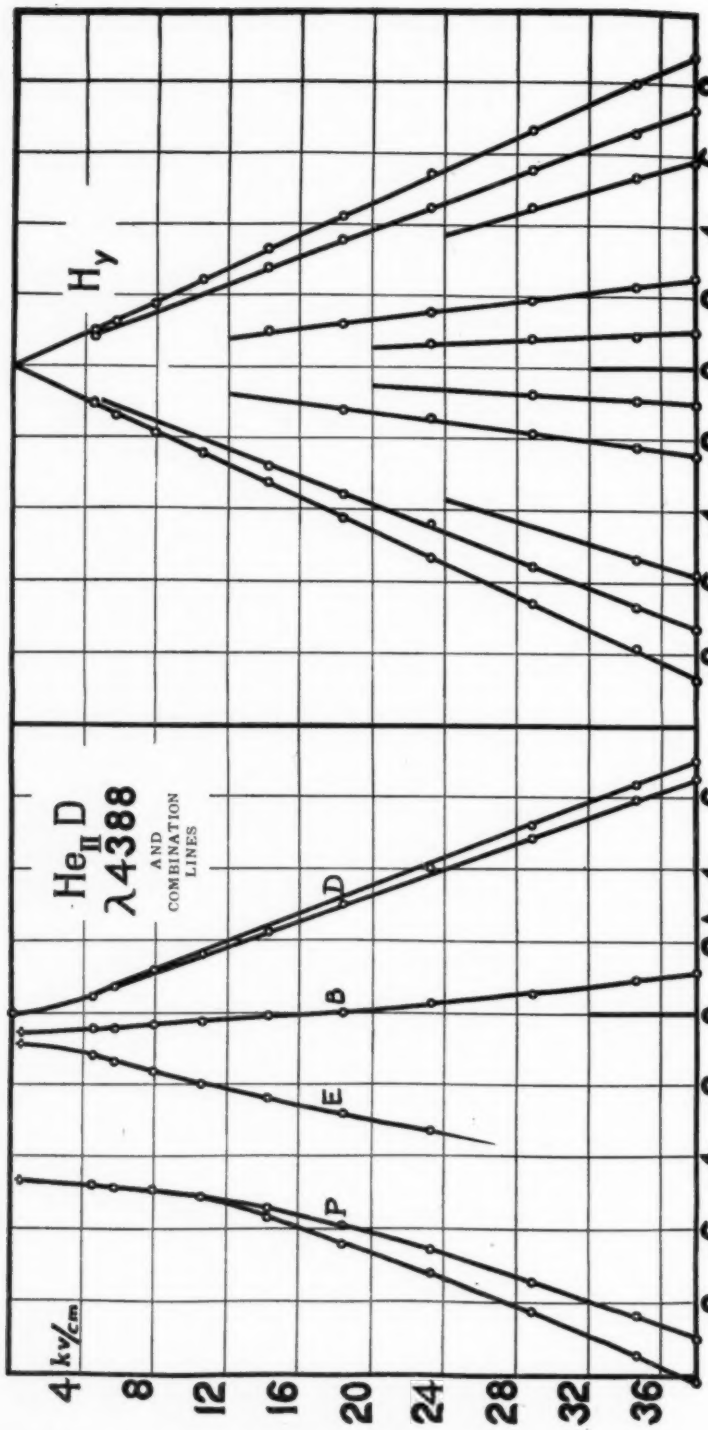

Fig. 4. He λ4388 group and Hγ in electric field.

these appear on Stark's plates at 104 kv/cm with a greater density than $5_{\pm 4}-2_0$. A similar statement may be made in regard to the corresponding perpendicular components of Hδ.

The Balmer series in very low fields. The rough analysis of Hβ, Hγ, and Hδ at very low fields (less than 3 kv/cm) shows that the red side of the affected line is more displaced from the strongest fine structure component and more diffuse than the violet side. Such relative displacements are observed with certainty only in the parallel components. The red side of each line is relatively diffuse, however, in both parallel and perpendicular images. The effect is apparent on all plates. It is not brought about by the slightly greater intensity of the apparently diffuse components.

It should be mentioned that according to Kramers' theory the fine structure line n_1-2_1 contributes but one Stark effect component. Presumably in the region in which the diffuse effect is actually observed, the theory claims that this strongest p-component crosses the other strong components on the red side of each Balmer line. The strong violet p-components are not so seriously disturbed. Theoretically the s-components present a more complicated structure in low fields. The displacements have not been calculated for every field strength throughout this region and for that reason one cannot predict the character of a rough analysis. One might guess, however, that for fields above 1.5 kv/cm the effect should agree with that observed.

Relative intensities of components of Hϵ. At the time Kramers' dissertation was published there were no observations with which to compare his theoretical estimates of the relative intensities of the Stark effect components of Hϵ. Two of the plates exposed in the glass spectrograph during this investigation show many components of this line. It is believed that a more complete analysis can be obtained through the use of the quartz spectrograph, and for that reason the present report is very brief. The relative intensities of the stronger inner components are very close to the predicted values. The strong outer p (and s) components at 60 kv/cm are relatively less intense than they were predicted to be at 100 kv/cm.

Parhelium

Near each diffuse line in parhelium there appears, in weak electric fields, a group of new lines. The extreme violet line in each group is a member of the series $2P-mP$. Direct measurements of the wavelengths at very low fields (0.2 kv/cm to 0.8 kv/cm) have been made on a plate exposed for ten hours in the glass spectrograph. In Table II these are recorded in the following manner. The first row gives the wave-

lengths for the series $2P-mP$. The next row marked "Series I" contains the wave-lengths of the lines which lie next those of the $2P-mP$ series. Continuing in this manner, "Series II" includes lines adjoining those in "Series I" and still nearer the D lines. Finally the D lines are measured as a means by which the fields may be determined more accurately at a later date.

TABLE II

Wave-lengths of combination lines in parhelium; $E<1$ kv/cm.

	$m=5$	$m=6$	$m=7$
$2P-mP$:	4383.29 (2)	4141.34 (1)	4007.47 (1)
"Series I" :	4387.07 (3)	4143.16 (1)	4008.55 (1)
"Series II" :	4387.42 (5)	4143.41 (3)	4008.90 (2)
"Series III":	———	4143.79 (5)	4009.19 (2)
D lines :	4388.01	4144.05	4009.41

The observations are tabulated as above merely as a matter of convenience. It is not believed that the lines in "Series I," for example, are members of an actual spectral series. One reason for such a conclusion is that they have an almost constant separation from the D lines. The additional experimental data contained in the following tables offer some aid to the problem of assigning the new lines to series.

TABLE III

Parallel components of the λ4388 group in electric field

E	Δλ from D line in zero field
38.0 kv/cm	7.03, 6.52, 1.11, −9.03, −10.12
34.7	6.36, 5.92, 0.92, −8.39, − 9.42
28.9	5.21, 4.83, 0.55, −7.45, − 8.27
23.3	4.02, 0.26, −3.30, −6.58, − 7.22
18.4	3.02, 0.03, −2.80, −5.90, − 6.41
14.2	2.26, −0.07, −2.36, −5.43, − 5.69
10.6	1.82, ——, −1.75, −5.11
7.9	1.20, −0.31, −1.62, −4.90
5.8	0.74, −0.42, −1.36, −4.83
4.6	0.47, −0.42, −1.17, −4.75
0.2*	0.08, −0.51, −0.86, −4.64

* Taken from another plate.

TABLE IV

λ4144 group in electric field; p and s-components

Field	Δλ from D line in zero field
34.8 kv/cm	p: 9.72, 4.52, −0.50, −5.61, −10.01, −11.78
	s: 9.77, 7.31, 4.39, 2.47, − 2.41, − 5.38, −7.28, −10.04, −10.98
26.8	p: 7.25, 3.12, −1.02, −4.74, −8.14, −9.21
	s: 7.41, 5.54, 3.39, 1.18, −1.92, −4.52, −5.70, −7.95, −8.62
15.2	p: 4.26, 1.65, −0.74, −3.66, −5.41
	s: 4.04, 2.99, 1.57, 0.79, −1.32, −3.35, −5.02
7.0	p: 1.83, 0.48, −0.93, −3.54
	s: 1.61, 0.49, −0.78, −1.70, −3.19
3.2	p: 0.87, −0.41, −2.61

TABLE V

4009 group in electric field p and s components

Field		Δλ from D line in zero field
34.8 kv/cm	p:	( )*, 8.04, 2.53, −8.08, −9.27, −11.71, −13.17
		( )*, 7.93, 5.65, 1.73, 0.22, −4.93, −7.66, −10.00, −12.41
26.8	p:	10.24, 5.78, 1.62, −6.37, −10.29
	s:	10.48, 8.32, 6.01, 4.25, 1.61, 0.19, −3.92, −6.12, −8.15, −10.34
15.2	p:	6.01, 3.36, 0.92, −4.21, −6.48
	s:	5.75, 4.74, 3.21, 2.34, −0.09, −2.37, −6.18
7.0	p:	2.74, 1.44, 0.10, −3.64
	s:	2.62, 1.27, 0.05, −1.26, −3.17
3.2	p:	1.35, 0.86, 0.10, −2.17

* Hidden by the λ4026 group. See Fig. 3.

TABLE VI

λ3614 group in electric field; p-components only

Field	$2S-5P$	$2S-5E$	$2S-5B$	$2S-5D$
5.0 kv/cm	λ3613.62			
9.0	13.40			
12.6	13.09	λ3615.35	λ3616.85	λ3618.42
18.8	12.42	14.83	16.96	19.28
28.2	11.23	14.28	17.32	20.51
34.4	10.38	13.90	17.56	21.29

λ3927 group. These lines are here observed in an electric field for the first time. They are too weak to permit accurate measurements. Three parallel components are seen with certainty—the two outside ones, and a third with a large displacement toward the red. The arrangement is quite similar to that of the parallel components of the 4144 and 4009 groups. There are two strong central perpendicular components as in 4144. The one on the red side has a weak companion. Spaced off toward the red is a cluster of about four components of nearly equal intensity. The components on the violet side are hidden by a band.

ORTHOHELIUM

TABLE VII

λ3820 group in electric field

Field		Δλ from d line in zero field
34.8 kv/cm	p:	12.78, 6.27, 1.48, −3.28, −8.06
	s:	12.47, 5.90, 1.70, −2.21, −3.28, −6.37, −7.93
26.8	p:	11.59, 4.94, 1.19, −2.51, −6.26
	s:	11.44, 4.49, 1.28, −1.79, −2.50, −5.01, −6.10
15.2	p:	10.53, 2.98, 0.70, −1.48, −3.70
	s:	10.13, 2.24, 0.36, −1.54, −3.60
7.0	p:	1.33, 0.25, −0.88, −2.08
	s:	1.07, 0.15, −0.82, −1.75
3.2	p:	0.62, 0.09, −0.57, −1.10

TABLE VIII

λ3705 group in electric field

Field		Δλ from d line in zero field
34.8 kv/cm	p:	12.98, 3.60, −1.11, −6.29, −10.97
	s:	12.41, 9.19, 4.49, −0.05, −1.23, −4.56, −6.13, −9.13, −10.34
26.8	p:	10.63, 3.05, −0.81 −4.71 −8.66
	s:	10.16, 6.67, 3.50, 0.06, −0.78, −3.37, −4.42, −6.96, −8.45
15.2	p:	7.73, 2.09, −0.36, −2.74, −5.14
	s:	7.09, 3.62, 1.59, −0.29, −2.20, −2.78
7.0	p:	1.13, −0.10, −1.18, −2.31
	s:	1.67, 0.84, −0.13, −1.06

λ4026 group. It has been reported that the central *s*-component in this group crosses another component at a high field. The details are not easily reproduced in a half-tone, but are clear on the plate. The central undisplaced line is produced in a manner already described. Up to the maximum field here considered, it is not crossed by any visible line. The central Stark effect component is for *2p−5b* and is displaced toward the red. Takamine has found that it crosses the undisplaced *d* line in very high fields. At about 20 kv/cm, however, the photograph shows a component breaking away from the *2p−5b* component already mentioned. This phenomenon is unusual. The branch component is displaced toward the violet. A similar effect makes its appearance at a lower field in the λ4388 group, where the corresponding component is displaced toward the red.

DISCUSSION

2P−mP series. It is an easy matter to pick out the lines in the series *2P−mP*. These lines were first measured by Nyquist (for $m=4,5$), and the classification was suggested by Liebert.[14] An error was made by the latter, who assumed that a strong line observed by Nyquist near λ4144 was *2P−6P*. It has been recorded as such in Fowler's tables. It is much stronger than the real *2P−6P* which lies a little toward the violet. The observed wave-lengths of *2P−6P* and *2P−7P* are recorded in Table IX. These lines are affected very little by weak electric fields.

2P−mB series. As Bohr has already pointed out, the calculated wave-lengths of the first two members of this series agree satisfactorily with those observed by Nyquist for the lines nearest 4922 and 4388. In the present experiments a fourth combination line is observed in the 4144 group which previously was known to contain three. This is

[14] G. Liebert, Ann. der Phys. **56,** 610 (1918)

believed to be the third member of the series $2P-mB$, and is so recorded in Table IX. With the discovery of this line, it becomes rather well established that each group of combination lines contains one more line than the preceding group. Thus while there is but one line near λ6678, the succeeding members of the diffuse series viz., 4922, 4388, and 4144 are accompanied in very low fields by 2, 3, and 4 lines respectively. Observations on the weak group 4009 are probably incomplete. In this group only four combination lines are observed with certainty.

The lines of the series $2P-mB$ are much more affected by weak fields than the members of $2P-mP$, and it is therefore difficult to get very

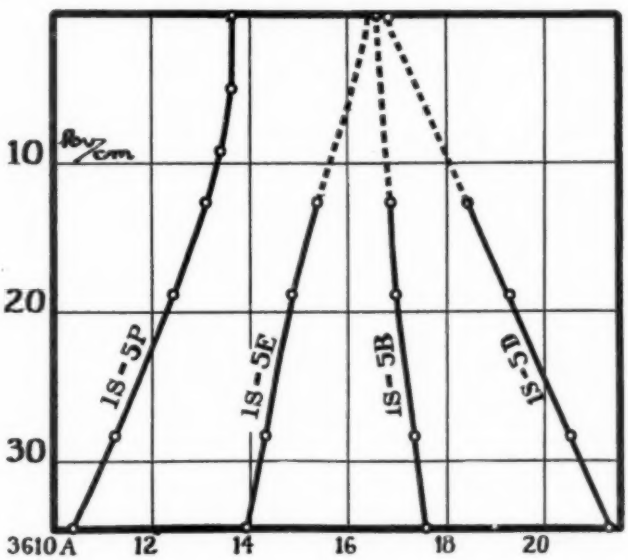

Fig. 5. λ3614 group in electric field.*

accurate measurements of the positions at zero field. Examination of the series in higher fields shows that there is a change in the direction of displacement with increasing order. The first member of the series is displaced toward the violet, whereas the second and all remaining members are displaced toward the red. Such an effect has been observed by Takamine and Kokubu[15] in the diffuse series of magnesium and by Takamine[16] in the diffuse and sharp series of copper. It is noted, also, that Kramers' theory of the connection between the fine structure and the Stark effect components in the Balmer series demands just this effect.

* In this figure "*1S*" should read "*2S*".

[15] T. Takamine and N. Kokubu, Mem. Coll. Sci. Kyoto, **3**, 173 (1918)

[16] T. Takamine, Astrophys. Journ **50**, 23 (1919)

Since $2P-6B$ is displaced toward the red and has been measured in a field wherein the D line 4144 was displaced 0.28A, its wave-length at zero field may be estimated by deducting half this amount from the observed value. This gives 4143.65A. Tschulanowsky has measured a single line in this group, believed by him to be $2P-6B$. Its wave-length at a very weak field was found to be 4143.53. There is a strong sharp line immediately on the violet side of $2P-6B$. It is displaced toward the violet, and in high fields is nearly symmetrically opposite $2P-6B$ (see Fig. 6). It is a little less affected by electric fields than is $2P-6B$; but assuming the same correction to hold, the estimated wave-length at zero field is 4143.55. This is in good agreement with Tschulanowsky's observation at 4143.53.

In taking the lines next the D lines as members of the series $2P-mB$, one is guided not only by the calculated wave-lengths, but by the fact that with increasing order there is an increasing similarity between the Stark effects in helium and in hydrogen. On the grounds of this very great similarity, it seems allowable to select the lines for each new series in the manner suggested by Kramers' theory. In making the selections in this way, no conflict in found with experimental evidence.

$2P-mE$ and succeeding series. There is now left in the 4388 group but one unassigned line and that, on the Bohr theory, must be $2P-5E$. According to the assumed arrangement, the line next $2P-6E$ is the first member of a new series $2P-mF$. Thus the line on the extreme violet side of each group, exclusive of lines in $2P-mP$, is the initial line of a new series. When a line is missing from a group, the Stark effects should act as a guide to identify those present in the analysis.

The following wave-lengths are observed in a low field.

TABLE IX

Observed and calculated wave-lengths of combination lines $2P-mQ$

	λ(obs.)	λ(calc.)	λ(calc.) − λ(obs.)
$2P-5P$	4383.29	4383.25	−0.04
$2P-6P$	4141.34	4141.32	−0.02
$2P-7P$	4007.47	4007.74	−0.27
$2P-5B$	4387.42	4387.59	−0.17
$2P-6B$	4143.79		
$2P-5E$	4387.07		
$2P-6E$	4143.41		
$2P-6F$	4143.16		

The connections between the additional lines observed in the 4009 group and the Stark effect components are not sufficiently clear to permit one to assign them to series.

The 2S−mQ series. The series *2S−mS* has been observed by Stark.[17] As only one displacement is recorded for each line, and that without specification of the polarization, it seems possible that this series may be plane polarized in agreement with the predicted nature of the corresponding series in hydrogen.

It has been noted that the parhelium groups already considered, *2P−mQ*, resemble the Balmer series in the electric field; but that certain components are missing from the helium patterns (see Figs. 4, 6, 7).

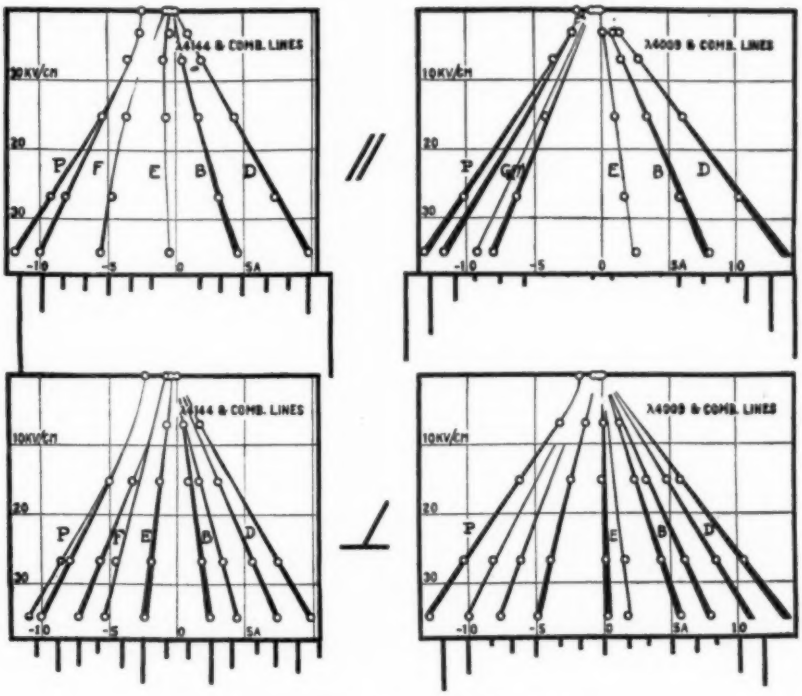

Fig. 6. Parhelium groups in electric field.

On the Bohr theory these should be associated with the lines emitted when the electron passes to the 2_1 orbit. For example, the components missing in the group 4388 (Fig. 4) should be found in the group 3614 (Fig. 5). It occurred to the writer that the very unusual curves which represent the relations between displacements and field strengths for the 4388 group made it seem probable that the new lines *2S−5Q* might be identified by a similar set of curves. The 3614 group was therefore examined at four field strengths, and the line 3614 was measured at two lower fields where the other lines presumably were too weak to

[17] J. Stark, Ann. der Phys. **56**, 577 (1918)

affect the plate. The observations are plotted in Fig. 5. By comparison with Fig. 4, it is found that the Stark effect for each line in the 3614 group is much like that for the corresponding line in the 4388 group. While the effects are not expected to be identical, they are unusual yet similar in the two groups. It is therefore believed that the two groups have a common set of initial orbits at zero field, and the violet lines have been classified accordingly in Table VI. By extrapolation it appears that at zero field the lines $2S-5D$ and $2S-5B$ have very nearly the calculated wave-lengths.

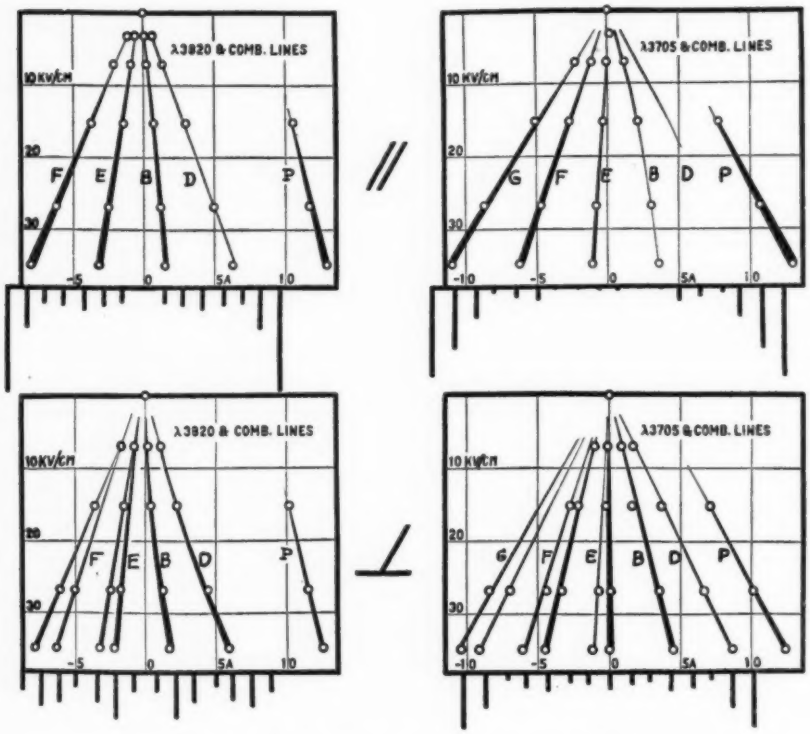

Fig. 7. Orthohelium groups in electric field.

Stark effect in parhelium. The Stark effects contributed by the two groups of lines $2S-mQ$, $2P-mQ$ ($Q=S,P,D,B,E,$ etc.) combine to present in parhelium patterns analogous to those found in the Balmer series. This seems to be rather good experimental evidence that the conditions in the Balmer series are substantially those predicted by Kramers. The number of components observed to originate in a given helium line is never greater than the number predicted for the corresponding fine structure line in hydrogen. On the other hand, the number

of components in helium is often less than might be expected. The separation of the components of a helium line is usually less than the separation of the corresponding components in hydrogen. It is therefore believed that in many cases more components would appear in higher fields (see $2p-5b$), or with greater dispersion. The s-component of $2p-6b$ seems double in some photographs; so does the p-component of $2P-6D$. Others may be relatively so weak that they fail to appear with those photographed.

Stark effect patterns. As a rule the observed Stark effect pattern is constant for the members of any one series of parhelium, but varies with the series. The sharp (n_1-2_2) and principal (n_2-2_1) series have but one p and one s-component. The series $2P-mQ$, $(n_{3,4,5}\ldots-2_1)$, have the same pattern. The $2P-mP$ series (n_2-2_2) is known to have two p and two s-components in the case of some lines. In others the pattern is apparently incomplete. The remaining series here considered might be expected to have two p and three s-components. The observed patterns are much simplified, however, and in many cases but one p and one s-component are found.

Vanishing components. Stark effect components which vanish or at least decrease in intensity with increasing field are rather numerous. If fact the representation of some of the new series seems to be limited, among the p-components, to a few orders. These lines do not vanish abruptly at a certain field strength. While remaining well defined, they decrease in intensity and appear to vanish at a field which varies with the exposure. As plotted in the diagrams, they are concave toward the position of the undisplaced line. Quite often the s-component is bent in the opposite direction, and the intensity increases with the field. In some photographs at least, the intensity of the p-component of $2P-6F$ passes through a minimum at a low field.

Orthohelium. As the orthohelium system is a system of doublets, one might expect to find evidence of this in the new combination lines which appear in the presence of an electric field. Tschulanowsky reports doublets near the diffuse lines 4472 and 4026. These he has classified as $2p_2-mb$ and $2p_1-mb$, $m=4,5$. The second term, as calculated from each line of the doublet, was found to vary appreciably. The wavelengths of the lines constituting the doublet near 4026 differed by 0.09A. The present photographs show two lines very near 4026. From their Stark effects, one is believed to be $2p_1-5b$ and the other $2p_1-5e$. They differ greatly as regards their behavior at high fields (see Fig. 2). At low fields they remain sharp ($2p_1-5b$ is unusually sharp) and approach one another up to the point where they become too weak to be distin-

guished. In a field such that Hδ has assumed twice its width at zero field, these lines are separated by 0.15A. There is no evidence of a line between them or on either side. It seems possible that Tschulanowsky's doublet may have been formed from these lines

The manner in which the doublet nature of these lines manifests itself in high fields will be described in a later paper.

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January 5, 1924.

THE SPECTRUM OF MERCURY BELOW THE IONIZATION POTENTIAL

JOHN A. ELDRIDGE

ABSTRACT

Spectrum of mercury excited by electrons of energy 7 to 10.4 volts.— When mercury vapor is bombarded by electrons of energy below the ionizing potential 10.4 volts, previous spectroscopic investigation has detected the emission of only the lines $1S-2p_2$ and $1S-2P$, whereas according to the Bohr theory there are many other lines which correspond to changes of orbit involving less energy change than 10.4 volts, which should be emitted line by line as the impacting energy is increased so as to be sufficient to take the electrons to the proper orbits. The failure to observe these lines is now shown to be due to the effect of space charge in lowering the energy of the impacting electrons except at the immediate surface of the anode, and by focussing light from the surface of the anode onto the slit of a quartz spectrograph, spectrograms have been secured showing the development of the spectrum of mercury in the stages predicted by the theory and at approximately the theoretical voltages. At 7 volts only $1S-2p_2$ appears, at 8.4 volts 4 new lines due to electrons returning from the $2S$ or $2s$ levels, at 8.9 volts 8 new lines due to electrons returning from the $3d_1$, $3d_2$, $3d_3$, $3D$ levels; at 9.9 volts 16 more lines; etc., in full agreement with the theory and with the photo-electric experiments of Franck and Einsporn.

THE complete spectrum of the normal mercury atom appears when the mercury vapor is ionized. Below the ionizing potential Franck and Hertz obtained a single line spectrum λ2536 and from analogy with other metals there can be little doubt that the line λ1849 also appears without ionization. According to the most obvious interpretation of the Bohr theory all of the lines should appear, group by group, below the ionization point, but other lines have not been observed.[1] Accordingly, a peculiar importance was formerly attached to the orbits $2p_2$ and 2P the orbits associated with these two lines. The electron could apparently be directly displaced by electronic collision from its normal position to these orbits but not to any others; the other orbits were apparently entered only by foreign electrons as they united with an ionized atom, and the complete spectrum, since it appeared at ionization, was naturally considered to be caused by the ionization of the gas.

[1] McLennan and Henderson, Roy. Soc. Proc. **91,** 485-491 (1915); McLennan and Ireton, Phil. Mag. **36,** 461-471 (1918). After the present work was begun Hertz announced somewhat similar results (Naturwissenschaften **11,** 778 (1923). Hertz did not use a quartz spectrometer and obtains therefore only four of the lines which are found in the present paper.

This somewhat unsatisfactory picture was discredited by the remarkable experiment of Franck and Einsporn. Using photo-electric rather than spectroscopic methods, they showed that the photo-electric current suddenly increased as the critical voltage for each of the known (as well as some unknown) orbits was reached. This result was extremely interesting but also somewhat puzzling, the most puzzling question being, if electrons are indeed displaced to these orbits without ionization, why do they not betray themselves to the spectroscopist? Until this was answered the theory was in a rather unsatisfactory state.

The answer seems to be that in the usual spectroscopic arrangement conditions are such that the space charge in the tube depresses the effective voltage below that of the electrodes and below that necessary to excite any but most easily excited lines. If conditions are such that the effect of space charge is minimized, all the lines come out group by group at these critical voltages, giving a beautiful demonstration of the truth of the fundamental Bohr theory.

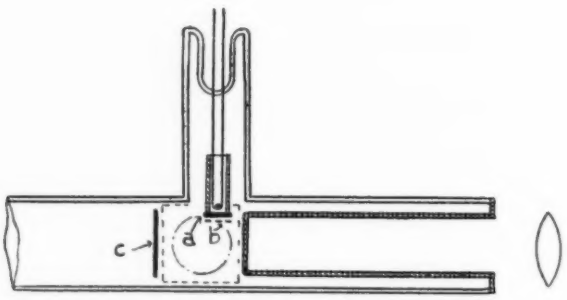

Fig. 1. Diagram of discharge tube.

The discharge tube used is shown in Fig. 1. The main tube was glass, about 3 mm in diameter, and was lined with nickel gauze to make the interior (ostensibly) a constant potential region. Re-entrant in one end was a quartz tube, the end being close to the region of discharge, and through this the spectrum could be observed with little absorption by the mercury vapor. The mercury was excited by slow electrons which, coming from the constant potential oxide coated platinum source *a*, were accelerated to the grid *b*, and entered the "constant potential region." The dashed circle in the figure represents a side tube extending several inches below the discharge chamber and forming a mercury well. Heating elements were provided about the mercury well and the discharge chamber to maintain a suitable vapor pressure (probably about .05 mm). The currents used were of the order of 1 milliampere.

It being the object of the experiment to detect, if possible, the spectrum below the ionization point, it was necessary to determine quite definitely the beginning of ionization. For this purpose the electrode *c* was placed behind the nickel grid at one end of the chamber. When the potential of this is kept equal to that of the thermionic source only positive ions can reach it. Such an electrode gives a small photo-electric current when illuminated, but this is always negligible in comparison with the positive ion current at ionization. The current to the electrode was measured as a function of the accelerating voltage (between source and grid). Fig. 2 shows that ionization set in when the impressed voltage reached 11 volts. The ionization potential of mercury is 10.4 volts; potential drops in the leads and contact potentials explain the discrepancy. The potentials as given later in this paper have been corrected by 0.6 volts to give the true potentials in the tube.

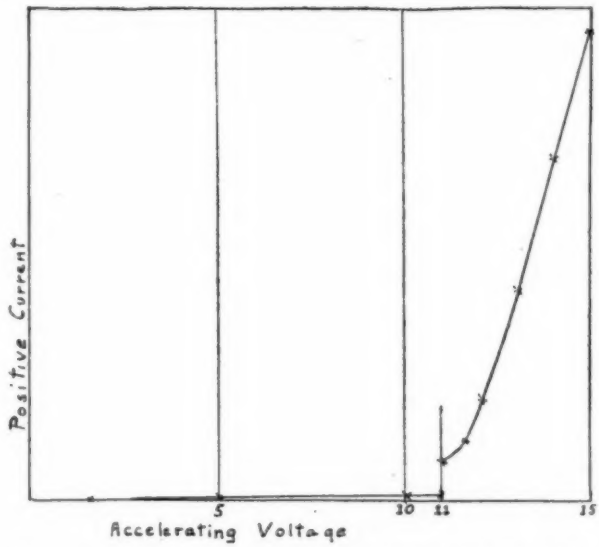

Fig. 2. Current-voltage curve showing ionization point.

While it was thought necessary to make this direct measurement of ionization, as a matter of fact the discharge suddenly alters its appearance when ionization sets in, so markedly that there can never be any doubt concerning the incidence of ionization. As the voltage is raised the tube appears to the eye at first dark; when the potential is within $2\frac{1}{2}$ volts of the ionizing potential, a green glow appears bordering the electrodes, at first very thin but extending further and further into the tube as the voltage is raised, the color changing somewhat at the same time. Just as the glow seems about to fill the entire tube, ionization

suddenly sets in (as measured by the galvanometer connected to c) with a complete change in the appearance of the tube. Above the ionization point, the visible glow is confined to a column proceeding from the cathode directly across the tube, the electron stream being sometimes so well directed as to preserve the pattern of the accelerating grid along the whole length of the column.

The obvious explanation of this behavior is that when there is no ionization the tube is so filled with negative space charge that only in their immediate proximity is the potential equal to that of the electrodes. Consequently only here are the various spectrum lines excited when the electrode reaches their respective critical potentials. The positive ions when they occur completely neutralize this space charge and allow light-producing collisions to occur at all points in the path of the electron.

Mercury Spectrum Below Ionization

In consequence of the space charge it is essential in examining the spectrum as a function of the exciting voltage, to focus upon the slit of the spectrometer light coming from the immediate proximity of the electrode. In the tube used one part of the gauze which lined the tube was flat and this was focused upon the spectrometer. A Hilger monochromator was adapted to serve as spectrometer by substituting a camera for the telescope; this gave sufficient dispersion for the purpose and was fairly rapid.

In Fig. 3 are shown spectrograms obtained with exciting electrons of different velocities, given in volts at the left of each spectrogram. To the right is given the usual energy level diagram so arranged that the various possible transitions are shown opposite the spectrogram to which they apply. In this diagram the vertical line *1S* represents the stable orbit of the valence electron; the other vertical lines representing the outer unoccupied orbits are drawn at distances proportional to the energies of these orbits, reckoning from the *1S* orbit as zero.[2] The scales at the bottom of the figure give the symbolic name of the orbit (Paschen's notation) and the energy of the orbit in volts. The symbols above the diagram N_k^j give the quantum numbers as assigned by Bohr, N being the total quantum number, k the azimuthal and j the inner quantum number.[3] It will be remembered that the selection principle allows all transitions in which k changes by one unit and in which j changes by 1 or 0 (except that the transition between orbits for each of which $j=1$

[2] For clearness it has been necessary to exaggerate the separations of the levels d_1, d_2, d_3 and D.

[3] Compare Bohr, Ann. der Phys. May 1923

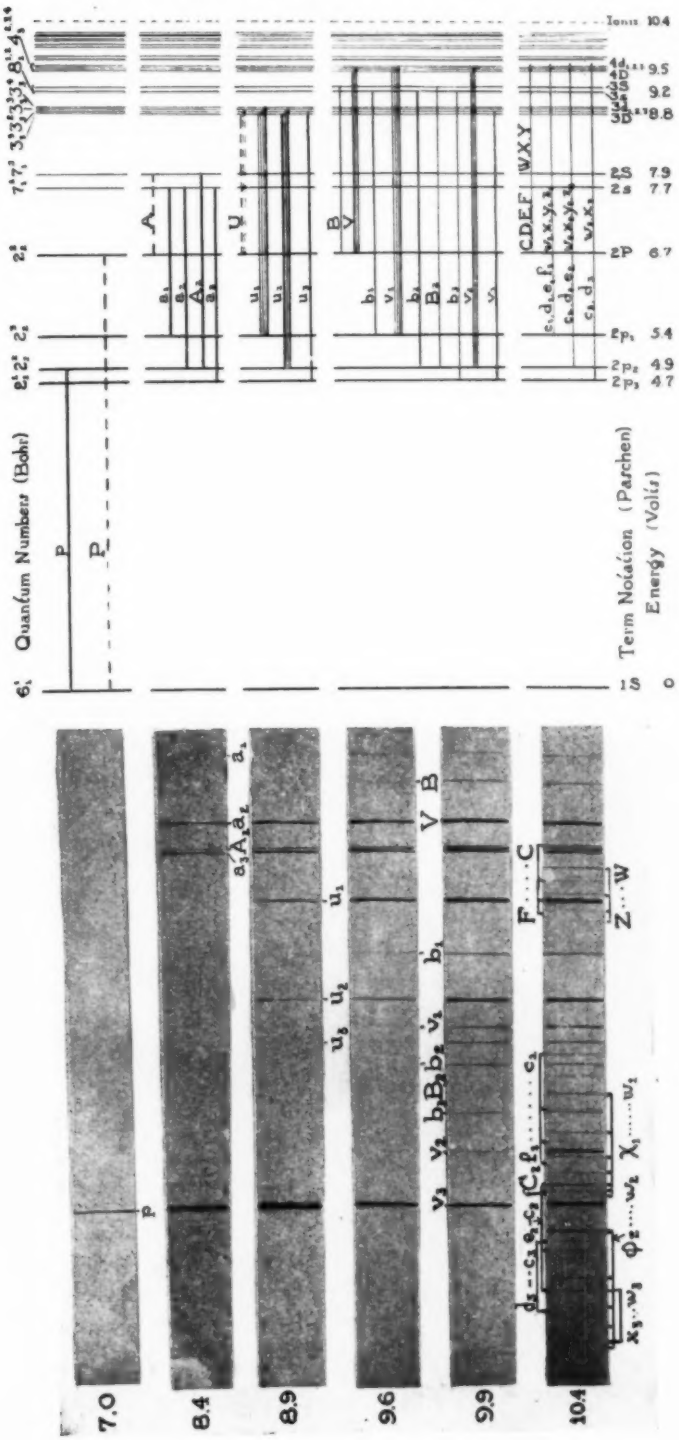
Ionis 10.4
9.5
9.2
8.8
7.9
7.7
6.7
5.4
4.9
4.7
0
Quantum Numbers (Bohr)
Term Notation (Paschen)
Energy (Volts)
7.0
8.4
8.9
9.6
9.9
10.4

Fig. 3.

is barred). To simplify the figure all levels of the p_1, p_2, p_3, or P type of higher order than the first have been omitted since there is no line involving levels of this type that falls within the range of sensibility of the photographic plates used. All other levels are represented and all light producing transitions permitted by the theory are given by the horizontal lines. Such of these transition lines as are dotted correspond to spectrum lines which fall in the infra-red or ultra-violet outside of the range of the plate and so are not represented in the spectrogram.

The notation which has been used should explain itself by reference to the energy diagram, but it may be summarized here:

2nd subordinate series

Triplets	$a_1 \ldots f_1$	represent	$(2p_1 - ms)$; $m = 2 \ldots 7$
	$a_2 \ldots e_2$	"	$(2p_2 - ms)$; $m = 2 \ldots 6$
	$a_3 \ldots d_3$	"	$(2p_3 - ms)$; $m = 2 \ldots 5$
Singlets	$A \ldots F$	"	$(2P - mS)$; $m = 2 \ldots 7$
Combination	$A_2 \ldots C_2$	"	$(2p_2 - mS)$; $m = 2 \ldots 4$

1st subordinate series

Triplets and combination	$u_1 \ldots \chi_1$	represent	$2p_1 - md_{1,2,3}$ $2p_1 - mD$	$m = 3 \ldots 10$
	$u_2 \ldots \phi_2$	"	$2p_2 - md_{2,3}$ $2p_2 - mD$	$m = 3 \ldots 9$
	$u_3 \ldots \chi_3$	"	$(2p_3 - md_3)$	$m = 3 \ldots 6$
Singlets	$U \ldots Z$	"	$(2P - mD)$	$m = 3 \ldots 8$

The topmost spectrogram shows the single line λ 2536, the only line which appears below 7.7 volts. The impacting electron has here enough energy to displace the atomic electron to the $2p_1$, $2p_2$, $2p_3$ or $2P$ orbits. The selection principle forbids the return from $2p_1$ or $2p_3$ and so the only lines which may be emitted at this voltage are $1S - 2P$ and $1S - 2p_2$ and of these the former falls too far in the ultra-violet to affect the plate. At 8.4 volts (the 2nd spectrogram) displacements of electrons to the $2s$ and $2S$ orbits are possible which result in the production of five more lines as shown in the diagram. The line $2P - 2S$, λ10139 is the strongest in the spectrum but is in the infra-red. The others appear in the spectrograms.

In the third spectrogram, excited by electrons falling from the $3d_1$, $3d_2$, $3d_3$ or $3D$ levels eight additional lines should appear. With the small dispersion used the multiplet character of the lines is not completely shown; on the original spectrograms three components of $2p_1 - 3d_{1,2,3}$ (D) are shown and two components of $2p_2 - 3d_{2,3}$ (D). In the next two spectrograms the lines from the $3s$, S levels are not completely separated from those originating in electrons coming from the $4d$, D levels and these two spectrograms are best considered together. The last spectrogram

shows the appearance of the spectrum just after ionization has set in, all the earlier lines of the subordinate series appearing.[4]

It will be realized that it is difficult to get sharp differentiation between the different groups of lines. This difficulty is due to three factors: (1) The velocity distribution of the electrons as they leave the source is nearly a volt. (2) The lens which focusses the tube upon the spectrometer slit is not achromatic; a blurred image of the light source is therefore obtained and when any new line appears as a narrow layer of light about the electrodes the image of this layer upon the slit is vanishingly weak. (3) It is likely that the probability of excitation of any state increases at least for a short range as the critical voltage is exceeded. This all makes it quite difficult to obtain the various lines with any suddenness as the critical voltages are reached. The best results were obtained by making the voltages as low as practicable and taking exposures of several hours.

Discussion of Results

It is very satisfying to have obtained the various groups of lines appearing at approximately the potentials predicted by the theory. The Bohr theory assigns certain energies to the different orbits. It is known from flourescent phenomena that light quanta of exactly these energy values can effect a displacement of the valence electron to these orbits (line absorption). The question arises whether it is actually possible for an electron with energy greater than that of some particular orbit to displace an electron to it. Hitherto the spectroscopic evidence has seemed to show that this was possible only in the case of the displacement $1S \rightarrow 2p_2$ and possibly in the case $1S \rightarrow 2P$. The present work, confirming the photo-electric results of Franck and Einsporn, shows that such a displacement is much more generally possible. It seems likely that a displacement of an electron from the normal ($1S$) orbit to any other is possible when the energy of an impacting electron equals or exceeds the energy of that orbit. It must be remarked however that the present experiment does not prove that this is the case because, for in-

[4] In the energy level diagram it has been impracticable to show all of the transitions from each of the outer levels corresponding to the many new lines in the last spectrogram. So by the single transition line shown terminating at the $2P$ level and drawn in the figure out to just beyond the $4d$ levels a multiplying of lines is to be understood starting respectively from the $4S$, $5D$, $5S$, $6D$, $6S$ etc. levels. All the lines given in the table are found but these are not all named in the energy diagram. The nomenclature here is obviously an extension of that in the upper spectrograms, C, D, E, F representing lines of the same series as A, B (i.e. $1P-mS$), W, X, Y, Z a continuation of the series whose earlier members are U, V, etc.

stance, if direct displacement were possible from the *1S* orbit to only some of the *d* orbits, nevertheless the other *d* orbits would become filled through collisions of the excited atom with neighboring atoms (collisions of the second kind of Rosseland and Klein.)

However this may be, it is certain that many, possibly all, of the lines of the spectrum are excited by electrons with velocities only slightly exceeding those calculated by the quantum relation. The transition $1S \rightarrow 2p_2$ has hitherto been considered specially prominent; in all inelastic collision experiments, even those of Franck and Einsporn where other deflection points were observed, it is this type of collision which dominates the whole shape of the curve. From the present work, on the other hand, it would appear that not only do the other lines appear below ionization but that the stronger of them are quite comparable in intensity with the line $1S - 2p_2$.

In addition to the inelastic collisions which Franck and Einsporn found corresponding to the most prominent spectroscopic terms there were a number of these collisions observed which had no spectroscopic counterpart. Of the collisions at lower voltage where the interpretation of their curve is quite definite, about half of those observed were in remarkable agreement with the spectroscopic terms, but half were equally definitely not to be associated with any known spectroscopic term. At that time with their results unsupported by spectroscopic observations, these anomalous types of collision could be considered as casting doubt upon the validity of the results; in view of the present work there can now, however, be little doubt as to their validity, and we must consider the meaning of those unexplained types of collision.

It appears possible that they are indeed real energy levels, whose orbits are quite incapable of functioning in spectroscopic emission since transitions both to and from them violate the selection principle. Such terms could not be detected by the spectroscopist, but only by an experiment such as that of Franck and Einsporn.

UNIVERSITY OF WISCONSIN,
February 2, 1924.

DURATION OF MOLECULES IN UPPER QUANTUM STATES

By Richard C. Tolman

Abstract

Values of rate of decay and mean life of atoms and molecules in upper quantum states calculated from data on the intensity of absorption lines.—By combining Füchtbauer's method of determining from the intensity of absorption lines the probability that a molecule will absorb a quantum of energy, with Einstein's views as to the mechanism of light absorption and emission, the following equation is derived for calculating the rate at which molecules jump from upper to lower quantum states:

$$A_{21} = \left(\frac{8\pi\nu^2}{c^2 N_1}\right)\left(\frac{p_1}{p_2}\right)\int_0^{+\infty} a\,d\nu$$

where A_{21} is the chance per unit time that a molecule will jump spontaneously from quantum state 2 to quantum state 1, ν is the frequency of the light emitted in such a jump, p_1 and p_2 are the a priori probabilities of quantum states 1 and 2, and a is the absorption coefficient of the substance measured under conditions such that N_1 is the number of molecules per unit volume in the lower quantum state 1. The integral $\int a d\nu$ is to be taken over the total effective width of the absorption line corresponding to the passage of molecules from quantum state 1 to quantum state 2. The mean life τ of molecules which decay from state 2 to state 1 is the reciprocal of A_{21}. Values of A_{21} and τ are calculated from existing data for the *mercury line* λ2537, for a number of lines belonging to the *alkali doublets*, for the *iodine line* λ5461, and for a very considerable number of lines belonging to the rotation-oscillation *spectra of the hydrogen halides*. The values obtained agree with the meager data made available by other experimental methods. From these results the following conclusions are drawn.

The mean life of molecules and atoms in upper quantum states may vary for different states at least over the range 1 to 10^{-3} seconds. The rate of decay is not a simple function of the frequency of the emitted light. The rate corresponding to the emission of a line of high frequency may be greater or less than that for a line of lower frequency. The data now available for the alkali doublets $1s-mp_1$ and $1s-mp_2$ indicate a higher rate of decay the smaller the change in total quantum number for the line under consideration. The rate of decay from a given mp_1 state is m times as great as from the corresponding mp_2 state (already stated in another form by Füchtbauer and Hofmann). In the case of the rotation-oscillation spectra of the hydrogen halides the rate of decay is greater for quantum states with one unit of oscillation and many of rotation, than for those with one unit of oscillation and only a few of rotation; and in the case of different molecules but the same quantum numbers the rate of decay is greater for the molecule with the greater frequency of oscillation.

Finally the possibility and method of calculating absolute values of A_{21} from the *Bohr correspondence principle* is indicated.

I. Introduction

THE interpretation of data on the positions of spectral lines has furnished us with relatively complete and precise information as to the energy contents of atoms and molecules in their different quantum states, and with considerable information as to the internal atomic or molecular configuration corresponding to these different states. At present, however, we have very little information as to the length of time that a molecule stays in a given quantum state, or as to the mechanism by which it jumps from one quantum state to another. Further knowledge in these directions may be of great assistance in promoting that reconstruction of theoretical physics which will be necessary for the reconciliation of wave theory and quantum theory.

In the present article we shall present a method of calculating from data on the intensity of absorption lines, the average time τ that molecules remain in an activated state before returning to their normal state by the re-emission of radiant energy. This time τ will then be calculated for a considerable number of different quantum jumps, the results will be compared with the meagre information provided by other methods of attack, and certain preliminary theoretical conclusions will be drawn.

The calculations are based on Füchtbauer's[1] method of determining from the intensity of absorption lines the probability P that a molecule will absorb a quantum of energy when illuminated with light of unit intensity. Füchtbauer's quantity P is evidently simply related to Einstein's[2] quantity B_{12} which is the probability that a molecule will become activated when surrounded by light of unit density, and this in turn can be shown to be related to A_{21} and B_{21} which are Einstein's probabilities, respectively, of free emission and of emission through negative absorption. The former of these A_{21} is the reciprocal of the mean life τ of the molecules in the upper quantum state.

The experimental data necessary for the calculations include a knowledge of the value of the absorption coefficient at every point across the width of the absorption line which corresponds to the quantum jump connecting the two states of the molecule in question, and the calculations possible at the present time are limited by the scarcity of such information. The work of Füchtbauer and his associates,[3] however, has provided us with some excellent data for certain quantum jumps in the cases of

[1] Füchtbauer, Phys. Zeits. **21,** 322 (1920)
[2] Einstein, Phys. Zeits. **18,** 121 (1917)
[3] Füchtbauer and Hofmann, Ann. der Phys., **43,** 96 (1914);
Bartels, Ibid, **65,** 143 (1921);
Füchtbauer, Joos and Dinkelacker, Ibid, **71,** 204 (1923)

mercury, sodium, caesium and iodine, while the work of Imes[4] gives us data for many quantum jumps for the hydrogen halides.

We may now proceed to the theoretical development, and shall need first of all to consider the factors which determine the width of a spectral line.

II. The Width of Absorption Lines

Absorption lines in gases and vapors have, as is well known, a small but finite width, the intensity of absorption falling off rapidly on both sides of an approximately central maximum. In terms of the quantum theory this distribution of intensities within the line finds its main explanation in the hypothesis that the molecules which absorb the light are not all of them in exactly the same condition, but are moving with various velocities relative to the on-coming light, and are variously affected by stray electromagnetic fields from neighboring molecules. The varying velocities of the molecules leads to a broadening of the line in accordance with the Doppler effect, and the result of the various electromagnetic fields is to affect the energy levels in the molecules and hence the magnitude of the absorbed quantum $h\nu$ and thus also lead to a broadening of the line.

The question as to what would be the width of an absorption line in case the absorbing molecules were all stationary and far enough apart to be unaffected by each others' fields is one of great theoretical interest for the quantum theory.[5] It is a question, however, which need not now detain us, since the actual width of the absorption lines which we shall consider is almost certainly much greater than the limiting width which would be produced by stationary isolated molecules, and we can neglect this limiting width in comparison with the broadening produced as described in the preceding paragraph.

III. Absorption Coefficient α and Probability of Activation P_{12}

Let us now investigate the intensities of absorption within an absorption line. Consider a beam of light of total intensity I measured in units of energy per unit area per unit time, falling on a layer of the

[4] Imes, Astrophys. J. **50**, 251 (1919)

[5] The extreme point of view of indivisible light quanta might lead to a value of zero for the width of line absorbed by stationary isolated molecules. From a less extreme point of view the width might have a very small value of the order calculated by quasi-classical methods. (See Epstein, Proc. Münchener Akad., p. 73, 1919. In any case, however, this limiting width is probably very small compared with the actual width produced with gases at moderate pressures.

absorbing medium of unit cross section and thickness dx. For the intensity of the light of a given frequency I_ν, we shall write,

$$I_\nu = dI/d\nu \tag{1}$$

Furthermore, in accordance with the discussion of the foregoing section, if N_1 is the total number of molecules per unit volume in the lower quantum state we may write

$$\delta N_1 = (\partial N_1/\partial \nu)\, d\nu\, dx \tag{2}$$

as the number of molecules in the layer in question which are so affected by their velocity and the field from neighboring molecules that they can respond to and absorb light of frequencies lying in the spectral range ν to $\nu+d\nu$. Hence if we assume that the chance of picking up a quantum of energy $h\nu$ is directly proportional to the intensity I_ν within the range ν to $\nu+d\nu$ and to the number of molecules that can respond, we may write for the energy absorbed per second within the range ν to $\nu+d\nu$ when light is passing through the layer

$$-d(I_\nu d\nu) = P_{12}\, h\nu\, I_\nu(\partial N_1/\partial \nu)\, d\nu\, dx \tag{3}$$

where P_{12} is the chance per unit time that a molecule will be activated under the action of light of unit intensity. Integrating with respect to x, we obtain for the intensity at any distance x

$$I_\nu = I_\nu^0\, e^{-P_{12}h\nu(\partial N_1/\partial \nu)x} \tag{4}$$

where I^0 is the intensity at $x=0$. If we write Eq. (4) in the form

$$I_\nu = I_\nu^0\, e^{-\alpha x} \tag{4'}$$

where α is the absorption coefficient for the frequency in question, we can then make the identification

$$\alpha = P_{12}\, h\nu\, (\partial N_1/d\nu). \tag{5}$$

If we now integrate α over the complete width of the spectral line, assuming P_{12} constant and neglecting the slight change in ν which will be allowable owing to the narrow effective width of the line, we obtain

$$\int_0^\infty \alpha d\nu = P_{12}h\nu \int_0^\infty (\partial N_1/\partial \nu)d\nu = P_{12}\, h\nu N_1$$

$$P_{12} = \frac{1}{N_1 h\nu}\int_0^\infty \alpha d\nu = \frac{\lambda}{N_1 hc}\int_0^\infty \alpha d\nu \tag{6}$$

where λ is the wave-length corresponding to ν.

IV. Discussion of the Probability of Absorption P_{12}

Except for a difference in symbolism, Eq. (6) for the probability of activation P_{12} is the same formula as that obtained by Füchtbauer,

although the method of derivation strives to attain somewhat greater clarity.[6]

In carrying out the integration, the probability P_{12} was taken as a constant independent of the frequency. This is presumably not strictly true since the molecules that absorb different frequencies are differently affected by the fields from neighboring molecules, and hence might be differently susceptible even to light of the proper frequency. Some idea of the possible effect of neighboring molecules on the value of P_{12} may be obtained from the experiments of Füchtbauer, Joos, and Dinkelacker[3] which show that the total value of the integral $\int a d\nu$ for the mercury line λ2537 decreases to about one half when nitrogen at a pressure of 50 atm. is added to the dilute mercury vapor. This indicates that neighboring molecules have only a moderate effect on P_{12} and we can safely regard the value obtained from Eq. (6) as a reasonable sort of average.

In the derivation of Eq. (6), presented in the preceding section it was tacitly assumed that all the light absorbed by the molecules in passing from the lower to the upper quantum state was permanently lost from the beam either by diffuse reradiation or by transfer through collisions of the second kind. The possibility arises, however, that molecules in the upper quantum state may return to the lower quantum state in such a way as to reinforce the primary beam by "negative absorption." This question will be considered more fully in a later section and it will be pointed out that for absorption experiments as usually performed the amount of "negative absorption" can be neglected.

For the experimental determination of the probability P_{12} in accordance with Eq. (6), we need a knowledge of the integral $\int a d\nu$. This can of course be most successfully obtained from an actual graphical integration under the experimental curve for the absorption coefficient. In the absence, however, of complete enough data for such graphical integration we may sometimes obtain an approximation by putting the integral $\int a d\nu$ proportional to the product of the maximum value a_m and the spectral width $\Delta\nu$ at which the value of a has sunk to one half its maximum value, in accordance with what may best be regarded as an empirical equation.

$$\int_0^\infty a d\nu = K\, a_m\, \Delta\nu. \tag{7}$$

If the Drude theory of absorption were correct, it has been shown by Füchtbauer,[1] changing to our notation, that the constant K would have the value $\pi/2$. It has been shown, however, by Bartels[3] that the value

[6] The quantities occurring in articles of Füchtbauer and his associates can be translated to ours with the help of the following equations: $i = I_\nu$; $n\chi = a\lambda/4\pi$; $P = P_{12}$, $\nu' = 2\pi\Delta\nu$; $nk = a\lambda/4\pi$; $b = \Delta\nu$.

$(\pi/2)a_m\Delta\nu$ is 36 per cent too large for the caesium line λ 3612, while the work of Füchtbauer and Hoffman[8] on λ 3877 under conditions to produce four times the broadening gave a value 38 per cent too large. Although this shows that the value $\pi/2$ may be seriously in error, it nevertheless indicates that for lines of similar origin, it will often be allowable to assume that K has the same value for the different lines. We can then calculate the ratio of the values of P_{12} for two different lines with the help of the equation

$$\frac{P_{12}}{P'_{12}}=\frac{N_1'h\nu'}{N_1h\nu}\frac{\int_0^\infty a d\nu}{\int_0^\infty a' d\nu'}=\frac{N_1'\nu'}{N_1\nu}\frac{a_m\,\Delta\nu}{a_m\,\Delta\nu'}=\frac{N_1'\lambda}{N_1\lambda'}\frac{a_m\,\Delta\nu}{a'_m\,\Delta\nu'}. \tag{8}$$

V. Relation of P_{12}, B_{12}, B_{21}, A_{21} and τ

The quantity P_{12} is the chance per unit time that a molecule will be activated by a beam of light of unit intensity I_ν, intensity being measured in units of energy per unit time, per unit cross section, per unit frequency range. If now the velocity of the light energy is c, it is evident that light of unit intensity would have the density $1/c$, where density u_ν is measured in units of energy, per unit volume, per unit frequency range.[7] Hence, if we denote by B_{12} the chance of activation per unit time under the action of light of unit density we obviously have

$$B_{12}=cP_{12}\ . \tag{9}$$

In order to show the relation between the quantity B_{12} first introduced by Einstein and his further quantities B_{21} and A_{21}, we shall next have to present a summary of his method of deriving the Planck radiation law.

Consider a molecule capable of existing in two quantum states with the energy contents ϵ_1 and ϵ_2, $\epsilon_2>\epsilon_1$, in equilibrium with black body radiation. For the number of molecules passing in unit time from state 1 to state 2 through the absorption of a quantum of energy, we have

$$-(dN_1/dt)=N_1u_\nu B_{12} \tag{10}$$

where N_1 is the number of molecules in state 1. For the number passing in the reverse direction we have

$$-(dN_2/dt)=N_2A_{21}+N_2u_\nu B_{21} \tag{11}$$

where N_2 is the number of molecules in state 2, A_{21} is the proportionality factor for spontaneous emission, and B_{21} the proportionality factor for emission through negative absorption, this latter process being introduced to preserve the analogy with the classical treatment.

[7] The velocity with which the *energy* is passing through the absorbing medium is taken as c, the same as the velocity of light in free space. See Sommerfeld, Phys. Zeits. **8**, 841 (1907)

If now at equilibrium the number of molecules going in unit time from state 1 to state 2 is equal to the number going in the reverse direction,[8] we have

$$N_1 u_\nu B_{12} - N_2 u_\nu B_{21} - N_2 A_{21} = 0. \tag{12}$$

In accordance with the Boltzman principle, and the Bohr relation between energy and frequency, however, we may write

$$\frac{N_1}{N_2} = \frac{p_1}{p_2} e^{(\epsilon_2 - \epsilon_1)/kT} = \frac{p_1}{p_2} e^{h\nu/kT} \tag{13}$$

where p_1 and p_2 are the a priori probabilities for states 1 and 2 and ν is the frequency of the absorption line accompanying the passage from state 1 to 2.

Substituting (13) in (12) and solving for u_ν, we obtain

$$u_\nu = \frac{A_{21}/B_{21}}{(p_1/p_2)\,(B_{12}/B_{21})\, e^{h\nu/kT} - 1} \tag{14}$$

Since u_ν must increase to infinity when T is infinite, it is evident that we must have the relation

$$(p_1/p_2)\,(B_{12}/B_{21}) = 1; \quad B_{21} = (p_1/p_2) B_{12} \tag{15}$$

so that equation (14) may be rewritten in the form

$$u_\nu = \frac{A_{21}}{B_{21}} \frac{1}{e^{h\nu/kT} - 1} \tag{16}$$

Furthermore in accordance with the Wien displacement law we have

$$u_\nu = \text{constant} \times \nu^3 \phi(\nu/T)$$

so that equation (16) becomes

$$u_\nu = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} \tag{17}$$

where $8\pi h/c^3$ may be regarded as the empirically determined constant.

This completes Einstein's deduction of the Planck radiation law. We have reproduced it here in order to obtain the relation between B_{12} and A_{21}. By comparison of Eq. (16) and (17) we see that

$$A_{21}/B_{21} = 8\pi\, h\nu^3/c^3$$

and by introduction of (15)

$$A_{21} = \frac{8\pi h \nu^3}{c^3} \frac{p_1}{p_2} B_{12} = \frac{8\pi h}{\lambda^3} \frac{p_1}{p_2} B_{12}. \tag{18}$$

[8] This assumption should be recognized as a distinct postulate and might be called the principle of *microscopic* reversibility. In the case of a system in thermodynamic equilibrium, the principle would require not only that the total number of molecules leaving a given quantum state in unit time shall equal the number arriving in that state in unit time, but also that the number leaving by any one particular path, shall be equal to the number arriving by the reverse of that particular path.

Since we have already shown the possibility of calculating B_{12} from absorption data we can now obtain values of A_{21} from the above equation or indeed by substituting Eq. (6) and (9) in (18) can obtain the following formula for the direct calculation of values of A_{21}

$$A_{21}=\frac{8\pi\nu^2}{c^2N_1}\frac{p_1}{p_2}\int_0^\infty a d\nu. \tag{18a}$$

The quantity A_{21}, however, as will be seen from Eq. (11), is the specific reaction rate for the monomolecular decay of molecules in state 2 in the absence of radiation. As is well known, the average life τ for molecules undergoing a monomolecular change can easily be shown equal to the reciprocal of the specific reaction rate, and we obtain

$$\tau=1/A_{21} \tag{19}$$

This completes the derivation of a method of calculating the mean life of molecules in an activated state from data on the intensity of absorption lines. In case the molecules can jump from state 2 to more than one lower state, it is obvious of course that the mean life will be the reciprocal of the sum of the specific reaction rates for the different paths.

VI. The Reinforcement of the Primary Beam by Negative Absorption

We have already called attention to the fact that our analysis of the nature of the absorption coefficient in an ordinary absorption experiment was based on the assumption that all the light absorbed by the quantum jump from state 1 to state 2 was permanently lost from the primary beam either by diffuse reradiation or by collisions of the second kind. The process of negative absorption, however, from analogy with classical mechanics, would presumably be of such a nature as to reinforce the primary beam, and we must assure ourselves that the magnitude of this reinforcement is negligible. This can easily be done.

It is evident from the discussion of the preceding section that the positive and negative absorptions will stand in the ratio

$$N_1B_{12}/N_2B_{21}=N_1p_2/N_2p_1$$

It can be shown, however, for the quantum states usually investigated, that N_1 is large compared with N_2 even when allowance is made for the molecules changed up into the higher quantum state by the light used for the experiment; p_2 and p_1, moreover, are of the same order of magnitude. Hence the reinforcement of the beam by negative absorption is negligible, as originally tacitly assumed.

VII. Values of P_{12} Calculated from Experimental Data

We may now proceed to the calculation of values for P_{12} for a number of cases where data are available. The values obtained are collected in

the fourth column of Table I. We give below sufficient data for the repetition of the calculations. Sources of the data are indicated by the initial letters of the authors' names already referred to,[1,3,4] which are inserted in brackets at the end of the data for a given spectral line.

A. Data

(in C. G. S. units unless otherwise specified).

Mercury, $\lambda = 2537$ A, $N_1 = 3.33 \times 10^{13}$, $(\lambda/4\pi) \int a d\nu = 5 \times 10^4$ (F. J. and D.)

Caesium, $\lambda = 3877$ A, $N_1 = 4.38 \times 10^{15}$, $(\lambda/4\pi) \int a d\nu = 5.64 \times 10^5$.
For use below, $\lambda a_m/4\pi = 3.74 \times 10^{-7}$, $2\pi\Delta\nu = 84.36 \times 10^{11}$. (F.)

$\lambda = 4593$ A, $N_1 = 8.49 \times 10^{13}$, $\lambda a_m/4\pi = 3.90 \times 10^{-7}$, $2\pi\Delta\nu = 3.92 \times 10^{11}$. (F).

$\lambda = 4555$ A, λa_m (for λ 4555) $= 3.05\ \lambda a_m$ (for λ 4593) under same conditions; and when corrected to same conditions $2\pi\Delta\nu = 4 \times 10^{11}$ for λ 4555 and $2\pi\Delta\nu = 3.85 \times 10^{11}$ for λ 4593 (F. and H.)

$\lambda = 3612$ A, P_{12} (for λ 3612) $= (1/3.69) \times P_{12}$ (for λ 3877). (B.)

$\lambda = 3617$ A, $\lambda a_m/4\pi = 2.33 \times 10^{-8}$, $2\pi\Delta\nu = 2.35 \times 10^{12}$; under the same conditions $\lambda a_m/4\pi = 11.65 \times 10^{-8}$, $2\pi\Delta\nu = 2.35 \times 10^{12}$ for λ 3612. (B.)

Sodium, $\lambda = 5890$ A, $N_1 = 2.22 \times 10^{12}$, $\lambda a_m/4\pi = 4.24 \times 10^{-7}$, $2\pi\Delta\nu = 3.46 \times 10^{11}$. (F.)

$\lambda = 5896$ A, $\lambda a_m/4\pi = 2.09 \times 10^{-7}$, $2\pi\Delta\nu = 3.68 \times 10^{11}$, under same conditions as for λ 5890. (F. and H.)

Iodine, $\lambda = 5461$ A, $N_1 = 3 \times 10^{16}$, $\lambda a_m/4\pi = 3.5 \times 10^{-7}$, $2\pi\Delta\nu = 0.6 \times 10^{11}$. (F.)

Hydrogen chloride,* pressure 1 atm., temperature about 20° C. (I.)

No. of line	λ	a_m	$\Delta\nu$
12	3.239×10^{-4}	0.01265	1.953×10^{11}
8	3.299	0.0970	1.178
3	3.394	0.2200	1.334
2	3.415	0.2265	0.879
1	3.439	0.1951	1.300
−1	3.489	0.2040	1.474
−2	3.516	0.3335	1.037
−3	3.544	0.3067	1.018
−8	3.699	0.09545	1.311
−12	3.846	0.01161	1.455

* The temperature of the gases in Imes' experiments is taken as 20° C for purposes of calculation, since the internal evidence of the article indicates that the work was done with the gases approximately at room temperature. The partial pressure p_{HF} of hydrogen fluoride *HF*, is unknown for two reasons. In the first place the total pressure of the gas is not stated although it was presumably in the neighborhood of one atmosphere, and in the second place hydrogen fluoride is known to be an associated gas at atmospheric pressure and room temperature. For this reason the results for hydrogen fluoride given in Table I all contain the unknown factor p_{HF}, but have of course perfectly good relative significance. Since p_{HF} is almost certainly less than 1 atm., it is evident that the values of P_{12}, B_{12} and A_{21} for hydrogen fluoride are greater than corresponding values for hydrogen chloride.

TABLE I[§]

(Quantities in C. G. S. units unless otherwise indicated)

Substance	Line	λ	P_{12}	B_{12}	p_1/p_2	A_{12}	τ
	n,j,k→n′,j′,k′,						
Mercury	6,1,1→2,2,2	2537 A	9.60 (10)^7	2.88 (10)^{18}	1/3	9.68 (10)^8	1.03 (10)$^{-7}$
Sodium	3,1½,1→3,2½,2	5890	7.74 (10)^8	2.32 (10)^{19}	1/3	6.21 (10)^8	1.61 (10)$^{-7}$
	3,1½,1→3,1½,2	5896	4.06 (10)^8	1.22 (10)^{19}	1/3	3.25 (10)^8	3.08 (10))$^{-7}$
Caesium	6,1½,1→7,2½,2	4555	6.67 (10)^7	2.00 (10)^{18}	1/3	1.16 (10)^8	8.64 (10)$^{-7}$
	6,1½,1→7,2½,2	4593	2.11 (10)^7	6.33 (10)^{17}	1/3	3.56 (10)^8	2.80 (10)$^{-7}$
	6,1½,1→8,2½,2	3877	8.44 (10)^6	2.53 (10)^{17}	1/3	2.37 (10)^8	4.21 (10)$^{-8}$
	6,1½,1→9,2½,2	3612	2.29 (10)^6	6.86 (10)^{16}	1/3	7.98 (10)^8	1.26 (10)$^{-8}$
	6,1½,1→9,1½,2	3617	4.56 (10)^5	1.37 (10)^{16}	1/3	1.58 (10)^8	6.33 (10)$^{-8}$
Iodine	——	5461	1.12 (10)^4	3.36 (10)^{14}	—	3.40 (10)^2	2.94 (10)$^{-3}$
	m,n→m′,n′						
HCl	12,0→13,1	3.239μ	43.0 (10)^4	129 (10)^{14}	12/13	57.7	0.0174
	8,0→9,1	3.299	4.65 "	14.0 "	8/9	5.69	0.176
	3,0→4,1	3.394	1.85 "	5.55 "	3/4	1.75	0.571
	2,0→3,1	3.415	1.46 "	4.38 "	2/3	1.21	0.829
	1,0→2,1	3.439	3.20 "	9.60 "	1/2	1.94	0.515
	1,0→0,1	3.489	3.85 "	11.6 "	∞ 1 0	∞ 4.48 0	0 0.223 ∞
	2,0→1,1	3.516	2.61 "	7.83 "	2	5.93	0.169
	3 0→2,1	3.544	2.05 "	6.15 "	3/2	3.41	0.293
	8,0→7,1	3.699	5.72 "	17.2 "	8/7	6.38	0.157
	12,0→11,1	3.846	34.9 "	105. "	12/11	33.1	0.0303
	23/2,0→25/2,1	3.239	23.3 "	69.9 "	12/13	31.3	0.0320
	15/2,0→17/2,1	3.299	3.11 "	9.33 "	8/9	3.80	0.263
	5/2,0→ 7/2,1	3.394	1.60 "	4.80 "	3/4	1.52	0.660
	3/2,0→ 5/2,1	3.415	1.33 "	3.99 "	2/3	1.10	0.910
	1/2,0→ 3/2,1	3.439	3.08 "	9.24 "	1/2	1.87	0.535
	3/2,0→ 1/2,1	3.489	2.05 "	6.15 "	2	4.77	0.210
	5/2,0→ 3/2,1	3.516	1.96 "	5.88 "	3/2	3.34	0.299
	7/2,0→ 5/2,1	3.544	1.83 "	5.49 "	4/3	2.71	0.369
	17/2,0→15/2,1	3.699	7.82 "	23.5 "	9/8	8.58	0.117
	25/2,0→23/2,1	3.846	61.1 "	183. "	13/12	57.5	0.0174
HF	6,0→ 1	2.395	6.65 (10)^4*	20.0 (10)^{14}*	6/7	20.5*	0.0488†
	2,0→3,1	2.475	3.77 "	11.3 "	2/3	8.19	0.122
	1,0→2,1	2.499	3.04 "	9.12 "	1/2	4.81	0.208
	2,0→1,1	2.578	2.35 "	7.05 "	2	13.6	0.0738
	5,0→4,1	2.671	4.04 "	12.1 "	5/4	13.1	0.0764
	11/2,0→13/2,1	2.395	3.69 "	11.1 "	6/7	11.4	0.0880
	3/2,0→ 5/2,1	2.475	3.17 "	9.51 "	2/3	6.88	0.145
	1/2,0→ 3/2,1	2.499	2.82 "	8.46 "	1/2	4.46	0.224
	5/2,0→ 3/2,1	2.578	1.97 "	5.91 "	3/2	8.52	0.117
	11/2,0→ 9/2,1	2.671	5.77 "	17.3 "	6/5	17.9	0.0557

§ In the abstract of this article which appeared in the Proc. Nat. Acad. *10*, 85 (1924) the values of A_{12} and τ for the members of the sodium and caesium doublets were inadvertently interchanged.

* These should be divided by the partial pressure of unassociated fluoride, p_{HF}.

† These should be multiplied by the partial pressure of unassociated fluoride, p_{HF}.

For line No. 1, $\int a d\nu = 4.572 \times 10^{10}$.

The moment of inertia of the molecule[9] is $J = 2.59 \times 10^{-40}$.

Hydrogen fluoride,* pressure p_{HF} atm. temperature about 20° C. (I.)

No. of line	λ	a_m	$\Delta\nu$
6	2.395×10^{-4}	0.0540	4.357×10^{11}
2	2.475	0.1470	3.875
1	2.499	0.1470	4.203
−2	2.578	0.1815	1.880
−5	2.671	0.0629	5.250

The moment of inertia of the molecule[9] is $J = 1.325 \times 10^{-40}$.

B. Method of Calculation and Reliability of Results

The value of P_{12} for mercury λ 2537 is probably the most reliable of any of those obtained. The value of N_1 is based on the known vapor pressure of mercury. The value of $\int a d\nu$ is based on experiments in which the width of the line was artificially increased by the presence of hydrogen, nitrogen, argon, or carbon dioxide at various pressures. Graphical integrations were performed with the data obtained at each pressure, and the final figure for $\int a d\nu$ was obtained by extrapolation to zero pressure (F. J. and D.). The value of P_{12} was calculated with the help of Eq. (6) and is quite possibly correct for mercury vapor at zero pressure to within 10 per cent.

The value of P_{12} for caesium λ 3877 is somewhat less satisfactory. The value of N_1 is again based on known vapor pressures, but the value of $\int a d\nu$ comes from one graphical integration with data obtained in a single experiment with added nitrogen at 30 atmospheres pressure (F). Extrapolation to zero pressure would lead to a value about one fourth higher if the effect of nitrogen on the ceasium line λ 3877 is the same as on the mercury line λ 2537. The final value of P_{12} was calculated with the help of Eq. (6).

The values of P_{12} for the other caesium lines and the two sodium lines, were calculated either directly or indirectly from the value for caesium λ 3877, with the help of Eq. (8) which assumes the same proportionality between $\int a d\nu$ and $a_m \Delta\nu$ for the different lines. This assumption is not serious compared with other uncertainties. Some of the values are in error owing to the wide extrapolation of vapor pressure necessary to get a value for N_1. (In making the calculations for all the caesium and sodium lines, Füchtbauer's values of N_1 cited above were decreased by 2.2 per cent, since he based them on an incorrect value of the Loschmidt number).

[9] Kratzer, Zeits. f. Phys. **3**, 289 (1920)

The value of P_{12} for iodine λ 5461 is approximate. It is calculated from Eqs. (6) and (7) assuming $K=\pi/2$.

In all the above calculations it was assumed that the number of molecules per cc in the lowest quantum state N_1 is equal to the total number per cc present. In view of the Maxwell-Boltzmann distribution law this assumption is presumably correct in the case of mercury, caesium, and sodium owing to the high energy levels of the upper quantum states for these atoms.

In the case of the rotation-oscillation spectra of the hydrogen halides, however, the different absorption lines are produced by molecules in different lower quantum states having small differences in energy level and the value of N_1 must be calculated for each of these lower states. These lower states differ from one another only in the number of units of angular momentum of the rotating molecule, that is in the value of the azimuthal quantum number m, the oscillation quantum number n being in every case zero.

Since two variants of the general theory of rotation-oscillation spectra[9,10] have been developed and complete certainty has not yet been reached as to which is correct, the calculations of P_{12} have been made according to both theories and somewhat different results obtained. According to the first theory, the azimuthal quantum number m, the a priori probabilities p_m, and the number of molecules in the successive quantum states take the values[11]

$$m=1,\ 2,\ 3,\ 4,\ \ldots \tag{19}$$

$$p_m=2m$$

$$N_m=Np_m\,e^{-m^2h^2/8\pi^2JkT}\Big/\sum_{m=0}^{m=\infty}p_m\,e^{-m^2h^2/8\pi^2JkT} \tag{20}$$

$$=N2m\,e^{-m^2h^2/8\pi^2JkT}(8\pi^2JkT/h^2)\ \text{(approx. at high temperatures)} \tag{21}$$

and according to the second theory the values[12]

$$m=1/2,\ 3/2,\ 5/2,\ \ldots,\ n-1/2,\ \ldots \tag{22}$$

$$p_m=2n$$

$$N_m=N\,p_m\,e^{-m^2h^2/8\pi^2JkT}\Big/\sum_{m=\frac{1}{2}}^{m=\infty}p_m\,e^{-m^2h^2/8\pi^2JkT} \tag{23}$$

$$=N2n\,e^{-(n-\frac{1}{2})^2h^2/8\pi^2JkT}(8\pi^2JkT/h^2)\text{(approx. at high temperatures)} \tag{24}$$

The values of N_1 for the two hydrogen halides were calculated using Eq. (21) and (24). The value of P_{12} for the hydrogen chloride line No. 1, λ 3.439μ, was calculated direct from Eq. (6) using the value of $\int a\,dv$ given above. This value was determined by performing a graphical integration on a plot of a against ν using the curve given by Imes[4] in

[10] Kratzer, Ergebnisse der Exakten Naturwissenschaften, **1**, 332 (1922)

[11] Reiche, Ann. der Phys. **58**, 637 (1919). See Case V.

[12] Tolman, Phys. Rev., **22**, 470 (1923)

Fig. 3 as a basis for obtaining values of α and ν. The values of P_{12} for all the other lines for the two halides were calculated with the help of Eq. (8), values of α_m and $\Delta\nu$ being determined from Figs. 3 and 7 in Imes. Imes' data on hydrogen bromide were not employed owing to uncertainty as to the concentration of the bromide which was mixed with an unknown excess of hydrogen.

The values of P_{12} thus calculated for the halides are subject to some uncertainty. Imes' experiments were primarily performed in order to determine the position of the lines rather than intensities of absorption and the reproduction of the absorption curves is on so small a scale as to make their use difficult. Assuming Imes' curves and their reproduction correct, the value of $\int \alpha d\nu$ for line No. 1 is probably correct within 25 per cent. A certain further uncertainty is introduced into the values of P_{12} for the other lines owing to their calculation on the assumption that $\int \alpha d\nu$ is proportional to $\alpha_m \Delta\nu$ instead of determining $\int \alpha d\nu$ by a graphical integration for each line. To test the probable error introduced by this cause, a graphical integration was performed for the hydrogen chloride line No. -8, λ 3.699μ. The graphical integration gave a value of P_{12} for this line 17 per cent lower than the value reported in Table I. Finally, it should be remembered, of course, that the values of α and ν are for the gases at atmospheric pressure and data for extrapolating to zero pressure are not available. Taking everything into consideration, the values of P_{12} for the hydrogen halides reported in the table are certainly of the right order of magnitude and large differences between the values for different lines undoubtedly correspond to actuality.

All values of P_{12} and dependent quantities are given in Table I to three significant figures, although two figures is perhaps all that the data even for the best cases warrant.

VIII. Values of B_{12}, A_{21} and τ

Using the values of P_{12} obtained as described above, values of B_{12}, A_{21} and τ have been calculated and are also given in Table I. The values of B_{12} are easily calculated with the help of Eq. (9).

In order to calculate the values of A_{21}, a knowledge of the a priori probabilities of initial and final quantum states is necessary. The second column in Table I gives the quantum numbers corresponding to the initial and final states for the particular line in question. The quantum numbers for mercury, sodium and caesium are assigned on the basis of Bohr's considerations,[13] n, j, k being respectively the total, inner and azimuthal quantum numbers for the lower quantum state, and n', j', k'

[13] Bohr, Ann. der Phys. **71**, 228 (1923)

for the upper quantum state reached by the absorption. The quantum numbers for the halides are assigned on the basis of the two variant theories already mentioned, m and n being respectively azimuthal and oscillation quantum numbers. The a priori probabilities for the quantum states of mercury[14] were taken as $3(2k-1)$; for sodium and caesium[14] as $2(2k-1)$; for iodine, in the absence of available information, as the same for both quantum states; and for the hydrogen halides as $2m$ on the basis of the first theory[11] and as $2(m+\frac{1}{2})$ on the basis of the second theory.[12] (Unity and infinity have also been inserted as possible values for the a priori probability of the state $m=0$, $n_2=1$ which has been so puzzling for the first theory.) Using the ratios p_1/p_2 obtained in the above manner, values for A_{21} have then been calculated with the help of Eq. (18).

The values of τ given in the last column of the table are merely the reciprocals of the corresponding values of A_{21}. In case the molecule can jump from the upper quantum state under consideration to more than one lower quantum state, the value of τ thus obtained is the mean life that the molecules would have if the particular jump considered were the only one possible. To get the actual mean life in such a case for all the molecules in the upper quantum state we should have to take the reciprocal of the sum of the values of A_{21} for all the different jumps possible. For the upper quantum states considered only one jump is possible in the case of mercury and sodium, but more than one is possible in the case of caesium (combination lines) and in the case of most of the hydrogen halide states.

IX. Comparison of Results with Other Experimental Data

It is a matter of great importance to compare the values of A_{21} and τ obtained in these calculations with those obtained by other if possible more direct experimental methods. Unfortunately direct methods of measuring these quantities are by no means easy to find and indeed this is one of the reasons for resorting to the method presented above.

One direct method for the measurement of τ which has been partially successful has been to measure the decay in the luminosity of canal rays whose velocity is known from the Doppler effect. By the use of this method Wien obtained $\tau=2.3\times10^{-8}$ sec. for both the β and γ lines of

[14] At the present stage of theoretical development, it is difficult to assign correct a priori probabilities to the quantum levels of mercury, sodium and caesium, but the above assignment is presumably of the right order of magnitude which is sufficient for our present considerations. In making the calculations the above expressions were taken as giving the a priori probability for a given k and any specified j. It is possible, however, that the expressions should really be taken as giving the total a priori probability for a given k and all the j's going with it (see Bohr, l. c. 13, pp. 276 and 279).

hydrogen, while Dempster obtained $\tau = 5 \times 10^{-8}$ sec. for the β line.[15] Wien also made some measurements by the canal ray method on oxygen and nitrogen lines, but apparently the method is not adapted for most substances, and no data are available for a direct comparison of canal ray results with ours. It is interesting to note, however, that the values of τ for *electronic* jumps obtained by the canal ray method fall in the region covered by our values of τ for roughly similar jumps.

Wood[16] has shown by direct measurements that τ for the mercury line λ 2537 must at least be less than 7×10^{-5} seconds, while Frank and Grotrian[17] by assuming that τ is of the order of 10^{-8} seconds have been able qualitatively to account for certain phosphorescence effects in mercury vapor observed by themselves and Phillips.[18]

Foote and Mohler[19] have shown that the value $\tau = 3 \times 10^{-8}$ for the D lines of sodium would account for Zahn's results on the energy emitted by a sodium flame, and this is in rough agreement with our value for the same lines.

The above recital practically exhausts previous information as to pertinent values of τ. It is evident however that the meager data available confirm the general correctness of our method of calculation.[20]

X. Qualitative Laws Governing the Rate of Decay of Activated Molecules

In spite of some uncertainty attaching to the results and the somewhat limited material available, it may nevertheless be useful to formulate tentatively some of the laws governing the rate of decay of activated molecules.

a. The mean life of molecules and atoms in upper quantum states may vary for different states at least over the range from 1 to 10^{-8} seconds.

[15] Wien, Ann. der Phys. **60**, 597 (1919); **66**, 229 (1921)
Dempster, Phys. Rev. **15**, 138 (1920). The interpretation of the canal ray results is by no means simple, since it necessitates a consideration both of the rate at which activated molecules are leaving the upper quantum state and the rate at which they then emit energy on their way to the lower quantum state. See Mie, Ann. der Phys. **66**, 237 (1921)

[16] Wood, Proc. Roy. Soc., A **99**, 362 (1921)

[17] Frank and Grotrian, Zeits. f. Phys. **4**, 89 (1921)

[18] Phillips, Proc. Roy. Soc. A **89**, 39 (1914)

[19] Foote and Mohler, "The Origin of Spectra," New York, 1922; pp. 165-169. Foote and Mohler actually used the value $\tau = 10^{-8}$, but their calculations were made on a basis which was tantamount to assuming unity for the ratio of a priori probabilities p_1/p_2. With the assumption used in the present article as to a priori probabilities their value of τ must be multiplied by 3.

[20] Since this article was first written, and the results of the calculations published in the Proc. Nat. Acad. **10**, 85 (1924), the value of τ obtained for the mercury line has been very satisfactorily confirmed by the calculations of Turner based on an entirely different method (see Phys. Rev. **23**, 464, 1924).

b. The rate of decay is not a simple function of the frequency of the emitted light. The rate corresponding to the emission of a line of higher frequency may be greater or less than that for a line of lower frequency.

c. The data now available for the alkali doublets indicate a higher rate of decay the smaller the change in total quantum number for the line under consideration.

d. In the case of the alkali doublets $1s-mp_1$ and $1s-mp_2$ (Paschen-Götze notation) the rate of decay from a given mp_1 state is m times as great as from the corresponding mp_2 state.[21] (This is merely another way of stating a conclusion already reached by Füchtbauer and Hofmann.[3])

e. In the case of the rotation-oscillation spectra of the hydrogen halides, the rate of decay is greater for quantum states with one unit of oscillation and many of rotation, than for those with one unit of oscillation and only a few of rotation.

f. In the case of the spectra of hydrogen chloride and hydrogen fluoride, for the same quantum numbers, the rate of decay is greater for the molecule with the greater frequency of oscillation.

With regard to the first of the qualitative laws stated above, the writer has had the pleasure of discussing the surprisingly low values calculated for the rate of decay of oscillating hydrogen chloride with Professor Paul Ehrenfest. The writer himself is inclined to believe that these slow rates of decay correspond approximately with reality, nevertheless certain other possibilities must be considered. The calculated rates of decay may come out too low either because of the use of too large values for N_1 or too small values for $\int a d\nu$. Since hydrogen chloride is not an associated gas, as is the case for hydrogen fluoride, the values of N_1 employed can not be incorrect for this reason. There is, however, the bare possibility that the hydrogen chloride molecule may have quantum states now unknown to us of low enough energy content so that an appreciable number of molecules are drawn away from the states of rotation for which we have calculated the values of N_1. As to the values of $\int a d\nu$ which were employed in the calculations, it should be pointed out that they were determined experimentally for hydrogen chloride at one atmosphere pressure and much larger values might be obtained at lower pressures, this would make the calculated chance for the emission of a quantum come out greater for an isolated molecule. The fact that the value for the mercury line λ 2537 is decreased by only fifty per cent when nitrogen at 50 atmospheres pressure is added might not rule out a much larger effect of collisions in the case of quantum jumps so different in nature. The

[21] It is possible that the difference in the intensities of the members of a doublet can be partly accounted for by a different assignment of a priori probabilities from that used in this article, and partly by an application of the correspondence principle in the way indicated by Sommerfeld and Heisenberg, Zeits. f. Phys. **11**, 131 (1922).

matter can of course be settled experimentally by determining $\int \alpha d\nu$ for hydrogen chloride gas at more than a single pressure. Before leaving this matter it should be pointed out that even if the values of A_{21} for oscillating hydrogen chloride molecules are as small as calculated, nevertheless the actual mean life of oscillating molecules is affected by the fact that more than a single downward quantum jump may be possible from the state 2 under consideration, and by the possibility of giving up energy by collisions of the second kind.

XI. Rate of Decay and Bohr Correspondence Principle

A theoretical method of predicting values of A_{21} would be very important. The Bohr correspondence principle has already proved its value for approximate calculations of the relative intensities of spectral emission lines,[22] which are closely related to relative values of A_{21}. The possibility of calculating absolute values of A_{21} at least approximately from the Bohr correspondence principle is an attractive one to consider. The most hopeful method of procedure to try would be to express the electric moment of the emitting molecule by a Fourier analysis, calculate by classical methods the rate of emission of energy due to the particular partial vibration that corresponds to the quantum jump under consideration, and equate this rate of energy emission, which would be ascribed by the classical theory to each individual molecule, to $A_{21}h\nu$ which is the average rate ascribed by the quantum theory to all the emitting molecules. The writer hopes to make this method of calculating values of A_{21} the subject of a later article.

XII. Conclusion

Before closing it should be pointed out that the results obtained in this paper are very intimately dependent on the point of view expressed by Einstein[2] in his 1917 paper, as to the emission and absorption of radiation. If the results thus obtained are always found to be in agreement with those obtained by other methods, it will certainly lend support directly to the Einstein point of view as to the emission and absorption of radiant energy by atoms and molecules, and hence somewhat indirectly to the extreme point of view of the existence of light quanta.

The writer wishes to emphasize the importance of further accurate determinations of values of $\int \alpha d\nu$, and the development of other methods for determining the rate of decay of activated atoms and molecules.

The writer wishes to express his thanks to Mr. James B. Friauf for assisting in the computations involved in the article.

Norman Bridge Laboratory of Physics,
Pasadena, California,
January 10, 1924.

[22] H. A. Kramers, "Intensities of Spectral Lines," Copenhagen Academy 1919.

ON THE RESISTANCE EXPERIENCED BY SPHERES IN THEIR MOTION THROUGH GASES

By Paul S. Epstein

Abstract

Kinetic theory of the resistance to a sphere moving through a gas.— (1) *Droplets small in comparison with the mean free path.* The high degree of accuracy achieved in the experimental determination of the law of motions of droplets through gases, makes a careful theoretical examination of the problem desirable. Assuming the usual Maxwellian distribution of velocities in the gas, the force exerted by the impinging molecules is found to be M where $M=(4\pi/3)Nma^2c_mV$, N, m, a, and c_m being the number per unit volume, mass, radius, and mean speed of the molecules and V the speed of the droplet. The force exerted by the molecules leaving the surface depends on how they leave. (1) For uniform evaporation from the whole surface, the force is $-M$; (2) for specular reflection of all the impinging molecules, $-M$; (3) for diffuse reflection with unchanged distribution of velocities, $-(13/9)M$; (4) for diffuse reflection with the Maxwell distribution corresponding to the effective temperature of the part of the surface they come from, $-(1+9\pi/64)M$, for a non-conducting droplet (4a), and $-(1+\pi/8)M$, for a perfectly conducting droplet (4b). Cases (1) and (2) can not be distinguished experimentally, but (2) is more probable physically. The experimental values agree with 1/10 specular reflection, case (2), and 9/10 diffuse reflection, case (4a) or (4b). For large values of l/a, the droplet behaves like a perfect conductor, case (4b). (2) *Comparatively large spheres.* The distribution of velocities is no longer Maxwellian because of the hydrodynamic stresses which can not now be neglected. The new law is derived (Eq. 47). The conditions at the surface of the sphere are discussed and it is shown that the diffusely reflected molecules have a Maxwellian distribution corresponding to the temperature and density of the gas, just as though they were reflected with conservation of velocity (specularly). The assumptions of Bassett are theoretically justified and a complete confirmation is obtained for the correction factor for Stokes' law $[1+0.7004\ (2/s-1)\ (l/a)]$ on which Millikan's conclusions are based, especially as to the percentage of specular reflection. (3) *Rotating spheres* are also considered in an appendix, and the values of the resistance are derived for various cases.

1. Introduction

THE high degree of accuracy achieved by Millikan and his pupils in the measurement of velocities of small spheres moving through gases[1] makes a careful examination of this problem from the theoretical point of view highly desirable. For the case of spheres which are large compared with the mean free path of the gas, we already possess quite

[1] See R. A. Millikan, Phys. Rev. **22**, 1, July 1923

a satisfactory theory, given by Millikan[2] himself. The opposite case of small spheres remained, however, unsettled. Some theoretical work was done by Langevin,[3] Cunningham,[4] and Lenard and his pupils[5] but the results of these authors were in partial disagreement with each other and in complete disagreement with the experimental facts. At the suggestion of Dr. Millikan I undertook, therefore, the analysis of this problem, and the first part of the present paper contains the results of my investigations in this respect. The values given by Lenard corresponding to various hypotheses as to the law of reflection of the molecules from the surface of the sphere, turned out to be correct from a mathematical point of view. From a physical point of view, however, it appeared that the hypotheses made by Lenard can scarcely be called probable or even permissible (section 5). Therefore two new hypotheses were worked out which seemed to me to be the most natural and the only probable ones. The two assumptions yield almost the same value for the resistance which is, moreover, in a very satisfactory agreement with the experimental value found by Millikan.

The second part is devoted to the theory from the kinetic point of view, of the resistance experienced by large spheres. An important paper of Millikan's,[2] already referred to, showed us for the first time the possibility of a theoretical understanding of his own correction to Stokes' Law by tying it up with the concepts of the external friction and the slip coefficient. His theory starts from a hydrodynamical resistance formula given by Bassett and contains as its only hypothetical element the assumption that the slip coefficient for a spherical surface of sufficiently large radius, is the same as for a plane surface. Though this assumption has *a priori* a high degree of probability and is vigorously supported by the experimental facts, it seems desirable to examine it also from the theoretical point of view, as well as the hypotheses underlying the theory of Bassett. The result is that Bassett's purely phenomenological assumptions are kinetically valid exactly to the same extent as this is necessary to justify Millikan's theory, so that the conclusions drawn by the latter are unimpeachable.

Part I. Resistance Experienced by Comparatively Small Spheres

2. *Distribution of velocities in the gas.* In this part we deal with spheres small compared with the mean free path. Such spheres will obviously

[2] R. A. Millikan, Phys. Rev. **21**, 217, March 1923
[3] Langevin, Ann. de Chim. et Phys. **5**, 266, 1905
[4] E. Cunningham, Proc. Roy. Soc. **83**, 359, 1910
[5] P. Lenard. Ann. der Phys. **61**, 672, 1920

exercise no influence on the distribution of velocities among the molecules, and the distribution will be that of a gas at rest, that is the Maxwell distribution: the number of molecules having the component of velocity parallel to the cartesian axes x, y, z between the values ξ, η, ζ and $\xi+d\xi$, $\eta+d\eta$, $\zeta+d\zeta$ is given by the expression

$$N_{\xi,\eta,\zeta}\, d\xi d\eta d\zeta = N\left(\frac{h}{\pi}\right)^{\frac{3}{2}} e^{-h(\xi^2+\eta^2+\zeta^2)} d\xi d\eta d\zeta \tag{1}$$

where N denotes the number of molecules per unit volume and h is an abbreviation of the following combination of the mass m of a molecule, the temperature T of the gas and the Boltzmann constant k

$$h = \frac{m}{2kT}. \tag{2}$$

In view of the Brownian movements, the velocity of a small sphere in a gas is not quite constant. However, it is not necessary to take into account these irregularities as they only change the resistance in the ratio $\mu/(m+\mu)$ where μ is the mass of the sphere, the difference of which from 1 is much too small to be observed. We shall, therefore, inquire as to the distribution of velocities from the point of view of an observer moving through the gas with a constant velocity having the components V_α, V_β, V_γ along the axes x, y, z respectively. This observer can regard himself as at rest and the molecules of the gas as moving with the velocities $\xi-\alpha V$, $\eta-\beta V$, $\xi-\gamma V$, instead of ξ, η, ζ. The velocity distribution for him will therefore be

$$N_{\xi,\eta,\zeta} = N\left(\frac{h}{\pi}\right)^{\frac{3}{2}} e^{-h[(\xi+\alpha V)^2+(\eta+\beta V)^2+(\zeta+\gamma V)^2]}. \tag{3}$$

If we limit ourselves to so small values of V that we need only to take into account the first power

$$N_{\xi,\eta,\zeta} = N\left(\frac{h}{\pi}\right)^{\frac{3}{2}} \{1-2hV(\alpha\xi+\beta\eta+\gamma\zeta)\} e^{-hc^2}, \tag{4}$$

where

$$c = \sqrt{\xi^2+\eta^2+\zeta^2} \tag{5}$$

denotes the absolute value of the velocity of a molecule.

We put together a few mathematical formulas which represent the chief instrument of the following computations:

$$\left.\begin{aligned} &\int_{-\infty}^{+\infty} e^{-h\xi^2} d\xi = \sqrt{\frac{\pi}{h}}; \quad \int_{-\infty}^{+\infty} \xi^2 e^{-h\xi^2} d\xi = \tfrac{1}{2}\frac{\sqrt{\pi}}{h^{3/2}}; \quad \int_{-\infty}^{+\infty} \xi^4 e^{-h\xi^2} d\xi = \tfrac{3}{4}\frac{\sqrt{\pi}}{h^{5/2}}; \\ &\int_0^{\infty} \xi e^{-h\xi^2} d\xi = \frac{1}{2h}; \quad \int_0^{\infty} \xi^3 e^{-h\xi^2} d\xi = \frac{1}{2h^2}; \quad \int_0^{\infty} \xi^5 e^{-h\xi^2} d\xi = \frac{1}{h^3}. \end{aligned}\right\} \tag{6}$$

3. *Number of molecules impinging on a surface element.* Making use of the distribution law (4), we ask how many of the molecules having velocity components between ξ, η, ζ and $\xi+d\xi$, $\eta+d\eta$, $\zeta+d\xi$ will strike in unit of time a surface element dS. We choose the x-axis as the direction of the normal to the element. The molecules we look for are those that at a given moment are lying in a cylinder constructed on the element dS as base in the direction of the velocity ξ, η, ζ with the length of the absolute value c of that velocity. The volume of this cylinder is equal to the product of the area of the base dS by the height $-\xi$, and as the number of molecules of the kind considered in unit of volume of the gas is $N_{\xi,\eta,\zeta}\, d\xi\, d\eta\, d\zeta$, the number of the impinging molecules will be

$$n_{\xi,\eta,\zeta}\, d\xi\, d\eta\, d\zeta\, dS = -N\left(\frac{h}{\pi}\right)^{\frac{3}{2}} \{\xi - 2hV(\alpha\xi+\beta\eta+\gamma\zeta)\xi\}\, e^{-hc^2} d\xi\, d\eta\, d\zeta\, dS. \quad (7)$$

For later applications we have still to compute the total number of impinging molecules n and the number of molecules $n_c dc$ striking the element with an absolute value of their velocity between c and $c+dc$. The number n we obtain by integrating $n_{\xi,\eta,\zeta}$ over all values of η and ζ and over all negative values of ξ:

$$n = \int_{-\infty}^{0} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} n_{\xi,\eta,\zeta}\, d\zeta = \frac{N}{2}\left(1+\sqrt{\pi h}\, \alpha V\right)\frac{1}{\sqrt{\pi h}}. \quad (8)$$

On the other hand, for finding n_c, we have to introduce polar co-ordinates by the integr

$$\xi = c\cos\psi, \quad \eta = c\sin\psi\cos\chi, \quad \zeta = c\sin\psi\sin\chi \quad (9)$$

and for the volume element $c^2 \sin\psi\, dc\, d\psi\, d\chi$,
so that instead of $n_{\xi,\eta,\zeta}\, d\xi\, d\eta\, d\zeta$ we get

$$n_{c,\psi,\chi}\, dc\, d\psi\, d\chi = -N\left(\frac{h}{\pi}\right)^{\frac{3}{2}} [\cos\psi - 2hVc\,(\alpha\cos\psi + \\ +\beta\sin\psi\cos\chi+\gamma\sin\psi\sin\chi)\cos\psi]c^3 e^{-hc^2}\sin\psi\, dc\, d\psi\, d\chi.$$

This expression we have to integrate over all directions of the impinging molecules, that is over χ from 0 to 2π and over ψ from $\pi/2$ to π.

$$n_c\, dc = \int_0^{2\pi} d\chi \int_{\pi/2}^{\pi} n_{c,\psi,\chi}\, d\psi = \frac{N}{\sqrt{\pi}}\, h^{3/2}\,(1+\tfrac{4}{3}hV\alpha c)c^3 e^{-hc^2} dc. \quad (10)$$

4. *Momentum transmitted by the impinging molecules.* Our object is to calculate the component of the momentum in a direction having the cosines α', β', γ' with the axes, that is transported by the totality of all molecules impinging on the surface element dS in unit of time. An individual molecule has in that direction the projection of momentum

$m(\alpha'\xi+\beta'\eta+\gamma'\zeta)$. Therefore, the momentum transmitted by all the impinging molecules is

$$m\int_{-\infty}^{0}d\xi\int_{-\infty}^{+\infty}d\eta\int_{-\infty}^{+\infty}(\alpha'\xi+\beta'\eta+\gamma'\zeta)n_{\xi,\eta,\zeta}\,d\zeta\,dS=$$
$$=-Nm\left\{\frac{\alpha'}{4h}+\frac{V}{\sqrt{\pi h}}(\alpha\alpha'+\tfrac{1}{2}\beta\beta'+\tfrac{1}{2}\gamma\gamma')\right\}dS.$$

Denoting the part of this expression depending on V by $M_s^{(i)}dS$ we find

$$M_S^{(i)}dS=-\left(\frac{NmV}{\sqrt{\pi h}}\right)(\alpha\alpha'+\tfrac{1}{2}\beta\beta'+\tfrac{1}{2}\gamma\gamma')dS. \tag{11}$$

Introducing instead of the constant h, the mean velocity $\bar{c}$ by means of the relation

$$\sqrt{\pi h}=\frac{2}{\bar{c}} \tag{12}$$

we obtain

$$M_S^{(i)}dS=-\tfrac{1}{2}Nm\bar{c}V\,(\alpha\alpha'+\tfrac{1}{2}\,\beta\beta'+\tfrac{1}{2}\gamma\gamma')dS. \tag{13}$$

If the element dS belongs to the surface of a sphere of the radius a moving through the gas with a velocity V, the normal to this element will form with V some angle θ. Let us choose the direction of the z-axis at right angles to the plane going through x and V; then we have $\alpha=\cos\theta$; $\beta=\sin\theta$, $\gamma=0$; and let us, moreover, determine the momentum communicated to the surface element in the direction V, ($\alpha'=\cos\theta$, $\beta'=\sin\theta$),

$$M_S^{(i)}dS=-\tfrac{1}{2}Nm\bar{c}V\,(\cos^2\theta+\tfrac{1}{2}\sin^2\theta)dS. \tag{14}$$

The total momentum received by the whole surface of the sphere from the impinging molecules is the integral of this expression over all the surface elements $dS=a^2\sin\theta\,d\theta\,d\varphi$

$$M^{(i)}=\int_0^{2\pi}\int_0^{\pi}M_S^{(i)}a^2\sin\theta\,d\theta\,d\varphi=-\tfrac{4\pi}{3}Nm\bar{c}a^2V. \tag{15}$$

This expression represents the *force of resistance* which a sphere experiences in its motion through a gas as far as the impinging molecules are concerned, or in other words the *reaction of the impinging molecules* on a sphere. To obtain the total resistance of the gas we must still add the reaction of the emerging (reflected or evaporated) molecules. We need not consider the terms independent of V because they represent the reaction in the absence of any motion of the sphere, which, of course, must vanish.

5. *Momentum of the emerging molecules. Old hypotheses.* We have now to calculate the momentum which a surface element receives from the molecules leaving it in unit time, that is the momentum which these molecules carry away, taken with the opposite sign. Of course, this

portion of the reaction depends entirely on the physical nature of the exchange of molecules between the gas and the spherical body. We have therefore to examine different possibilities.

Case (1). Uniform evaporation from the whole surface of the sphere. Under this assumption the gas molecules hit the sphere according to the law of section 3, but are condensed at its surface and re-evaporated at the same rate from every surface element, independently of its position. It is obvious that the loss of momentum occurs in this case perfectly symmetrically, so that the total force of reaction due to the emerging molecules is zero $M_1^{(e)}=0$

and
$$M_1=M_1^{(e)}+M^{(i)}=-\tfrac{4}{3}\pi\ Nm\bar{c}\,a^2V. \tag{16}$$

This assumption was examined by Lenard[5] with the same result, and by Cunningham who, however, obtained double the value.[6] It can hardly be regarded as physically probable, as the number of impinging molecules is quite different in every point of the sphere, and a rapid equalization would require a high fluidity of the surface layer.

Case (2). Specular reflection. Every molecule retains after the reflection its old values of η and ζ, but changes the sign of ξ. The reflected molecules will, therefore, have a stream velocity with the opposite sign of the x-component of V; instead of α we have to write $-\alpha$. We have to substitute in (11) $\alpha=-\cos\theta$, $\beta=\sin\theta$, while α' and β' undergo no change ($\alpha'=\cos\theta$, $\beta'=\sin\theta$), and in view of the opposite sign of the whole expression, we get

$$M_S{}^{(i)}dS=\tfrac{1}{2}\,Nm\bar{c}V\,(\cos^2\theta-\tfrac{1}{2}\sin^2\theta)dS.$$

The integration over all the surface of the sphere gives

$$M_2{}^{(e)}=a^2\int_0^{2\pi}\int_0^{\pi}M_S{}^{(e)}\sin\theta\,d\varphi\,d\theta=0.$$

Again the emerging molecules exercise, on the whole, no force of reaction at all, and we get for the resistance the same value as before

$$M_2=M_2{}^{(e)}+M_2{}^{(i)}=-\tfrac{4}{3}\pi Nm\bar{c}\,a^2\,V, \tag{17}$$

in agreement with the results of Langevin, Lenard, and Cunningham.

[6] Cunningham gives a detailed computation only for the case of specular reflection. With respect to condensation he says: " . . . the mean impulse is found to bear to that previously found the ratio of

$$\int_0^{\pi}(1+\cos^2\theta)\,\sin\theta\,d\theta \text{ to } \int_0^{\pi}2\,\cos^2\theta\,\sin\theta\,d\theta,$$

that is, exactly the double." It is true that, if one works out the two cases following Cunningham's method of computation, the parts of the momentum integrals proportional to the velocity V contain the factors $(1+\cos^2\theta)\,\sin\theta\,d\theta$ and $2\,\cos^2\theta\,\sin\theta\,d\theta$. However, previous to the integration with respect to $d\theta$, one has to carry through an integration with respect to another variable the limits of which depend themselves on θ and on V. By this the ratio of the two impulses is entirely changed and turns out to be 1.

The fact that the resistance is the same in both cases removes the basis of all the discussions about the factor $f+2(1-f)$ introduced by Cunningham, where f denotes the fraction of molecules reflected specularly and $(1-f)$ the fraction of uniformly evaporated molecules. The correct form of this expression is $f+(1-f)=1$, so that it is impossible to discriminate between the two cases by observations on mobility.

Case (2a). Radial reflection. This hypothesis has been used by McKeehan, Gaede and Lenard and consists in the assumption that every molecule retains after reflection the absolute value of its velocity but is reflected in the direction of the normal to the surface. Let us consider the reaction of the $n_c dc$ reflected molecules having velocities between c and $c+dc$. As each of them carries away the radial momentum mc, the total momentum carried away by this group from the element dS will be $mcn_c dcdS$, and the reaction on the element dS by all the molecules emerging from it with any velocity will be, according to (10),

$$M_S^{(e)}dS=-\tfrac{4}{3}\,N\,\frac{h^{5/2}}{\sqrt{\pi}}mV\alpha\int_0^\infty c^5 e^{-hc^2}dc\;\;dS=-\tfrac{4}{3}\frac{Nm}{\sqrt{\pi h}}\;\alpha V dS.$$

As in section 4, α has the value $\cos\theta$. This force is directed normally; in order to get the total force in the direction of the velocity V, we have to take the projection in this direction by multiplying by $\cos\theta$, and integrate it over the whole surface of the sphere. Using, moreover, relation (12)

$$M_{2a}^{(e)}=-\tfrac{2}{3}\,Nm\bar{c}a^2V\int_0^{2\pi}\int_0^{\pi}\cos^2\theta\sin\theta\,d\varphi d\theta=-\tfrac{8\pi}{9}\,Nma^2V\,\bar{c}.$$

The total force is therefore

$$M_{2a}=M_{2a}^{(e)}+M^{(i)}=-\tfrac{20}{9}\pi\,Nm\bar{c}\,a^2V. \tag{18}$$

It is explained in a preceding paper by Millikan[1] that such a law of reflection would violate the second law of thermodynamics.

Case (3a). Diffuse reflection according to Lenard. As in (2a) the molecules retain after reflection the absolute values of their respective velocities, but are distributed in all directions so that for every velocity there emerges in a solid angle $d\Omega$ a number of molecules proportional to the value of $d\Omega$. The mean momentum carried by a molecule of the velocity c is, therefore, in the direction of the normal and has the absolute value

$$\frac{m}{2\pi}\int c\cos\psi\,d\Omega=\frac{m}{2\pi}\int_0^{2\pi}\int_0^{\pi/2}c\cos\psi\,\sin\psi\,d\chi\,d\psi=\tfrac{1}{2}mc.$$

The whole difference between this case and the case of radial reflection is, therefore, that we have to multiply n_c by $mc/2$ instead of mc, so that

$$M_{3a}^{(e)} = \tfrac{1}{2}\ M_{2a}^{(e)} = -\tfrac{4\pi}{9} Nm\bar{c}a^2 V. \tag{19'}$$

The total resistance becomes in this case

$$M_{3a} = M_{3a}^{(e)} + M^{(i)} = -\tfrac{16\pi}{9} Nm\bar{c}a^2 V. \tag{19}$$

However, it is easy to see that such a hypothesis is no less in contradiction with the principle of entropy than the last one. The distribution of directions adopted by Lenard is *not a random distribution* in the statistical sense. Indeed, the principles of statistics tell us that in a homogenious gas, among *the molecules contained in a given volume* every solid angle has equal probability. The distribution of velocities among *the molecules coming from a surface element* is quite a different matter and is found by the construction of a cylinder on the surface element, as shown in section 2. The volume of the cylinder turned out there to be $\xi\, dS = c\cos\psi\, dS$, so that the probability of a given solid angle $d\Omega$ is proportional not only to this value but also to $\cos\psi$; it is therefore

$$\frac{\cos\psi\, d\Omega}{\int d\Omega} = \tfrac{1}{2\pi}\cos\psi \sin\psi\, d\chi\, d\psi. \tag{20}$$

That the assumption of Lenard is not permissible appears most clearly if we consider the reaction on a surface element at rest ($V=0$). According to (10) this will be

$$M_S^{(e)} dS = -\tfrac{1}{2} m \int_0^\infty c n_c\, dc\, dS = -\tfrac{3}{16}\,\frac{Nm}{h}\, dS,$$

while in the case of specular reflection we have from (7)

$$M_S^{(e)} dS = -m \int_0^\infty d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \xi\, n_{\xi,\eta,\zeta}\, d\zeta = -\frac{Nm}{4h}\, dS.$$

The difference amounts to $NmdS/16h$, or to one eighth of the pressure of the gas. Taking a disk with a diffusely reflecting surface on one side and a specularly reflecting on the other, we should therefore be able to obtain a perpetual motion of the second kind.

6. *New hypotheses as to the physical nature of molecular impact.* Of course, the streaming of the impinging molecules has a certain influence on the distribution of directions among the reflected ones, but this one usually takes into account by saying that there is a certain proportion of specular reflection. For the remainder of the reflected molecules we are looking for a law of *random distribution* of directions independent of the velocity of the impinging ones and symmetrical with respect to the normal. There is no doubt whatever that the only thermodynamically permissible law is that of formula (20), so that the mean momentum

carried away in the normal direction by molecules having the velocity c is given by

$$\frac{mc}{2\pi}\int_0^{\pi/2}\int_0^{2\pi}\cos^2\psi\,\sin\psi\,d\chi\,d\psi=\tfrac{2}{3}\,mc.$$

As to the distribution of the absolute values of velocities among the emerging molecules many assumptions are thermodynamically possible, but only the following two seem reasonable.

Case (3). Diffuse reflection with conservation of velocity. The molecules retain the distribution which they bring with them, that given by formula (10), or in other words, every molecule retains after reflection its former velocity. The only difference from case (3a) is that we have to take as mean momentum not $mc/2$ but $2mc/3$ so that the result (19′) is increased in the proportion 4/3:

$$M_3^{(e)}=-\tfrac{16\pi}{27}Nm\bar{c}\,a^2V$$

and

$$M_3=M_3^{(e)}+M^{(i)}=-\tfrac{52\pi}{27}Nm\bar{c}\,a^2V. \tag{21}$$

Case (4). Diffuse reflection with accommodation. The hypothesis of conservation of velocity treats the surface of a solid or liquid body as if it were rigid. We know, however, that the collision of the gas molecules in reality occurs with the individual molecules or atoms constituting that surface and results in an exchange of momentum and energy with the latter. The assumption which is physically most satisfactory is, therefore, that the gas molecules in being reflected accommodate themselves either completely or partially to the temperature of the reflecting surface. If T is the temperature of the gas and T' that of the surface, then the hypothesis usually made is that the reflected molecules possess a temperature T'' given by the formula

$$T''-T=\sigma\,(T'-T) \tag{22}$$

where σ is a constant smaller than 1 called the "coefficient of accommodation." We shall call T'' the "effective temperature" of the surface. For all our purposes it is quite immaterial whether it happens to coincide with the true temperature or not, that is, whether we have complete or partial accommodation. We shall, therefore, assume that all the impinging molecules are reëmitted from the same surface element which they strike and that in leaving the surface they possess, with respect to their velocities and directions, a Maxwell distribution corresponding to the effective temperature of the part of the surface they come from. Two sub-cases must be distinguished.

Case (4a). The sphere is a perfect thermal non-conductor. The energy balance must then be maintained for every surface element individually. Its temperature will increase or decrease until the energy carried off by the emerging molecules will be just equal to the energy brought by the impinging ones. The constant h of the distribution law will, therefore, be a function of the position on the surface of the sphere; as the difference from the normal value will be but slight, we will write $h+h'$ instead of h, with the understanding that h' is a small quantity the square of which can be neglected. We have to assign to the number of molecules emerging from a surface element dS with velocities between ξ, η, ζ and $\xi+d\xi$, $\eta+d\eta$, $\xi+d\zeta$ an expression of the same type as the first term of (7)

$$n^{(e)}{}_{\xi,\eta,\zeta} = Ce^{-(h+h')c^2}\xi = C\xi\{1-h'(\xi^2+\eta^2+\zeta^2)\}e^{-hc^2}.$$

The coefficients C and h' are determined by the two conditions, conservation of number and conservation of energy. The first condition is satisfied if the total number of emerging molecules

$$n^{(e)} = \int_0^{\infty} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} n^{(e)}{}_{\eta,\zeta,\xi}\, d\zeta = \frac{C\pi}{2h^2}\left(1-\frac{2h'}{h}\right)$$

is equal to the number of impinging ones given by (8):

$$\frac{C\pi}{h^2}\left(1-\frac{2h'}{h}\right) = \frac{N}{\sqrt{\pi h}}(1+\sqrt{\pi h}\ \mathfrak{a}\ V). \tag{23}$$

The second condition tells us that the energy transport to the element dS

$$\tfrac{1}{2}m\int_{-\infty}^{0} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} (\xi^2+\eta^2+\zeta^2)n_{\xi,\eta,\zeta}\, d\zeta = \frac{m}{2h}\,\frac{N}{\sqrt{\pi h}}(1+\tfrac{5}{4}\sqrt{\pi h}\,\mathfrak{a}V) \tag{24a}$$

must be equal to the energy transport from it

$$\tfrac{1}{2}m\int_{0}^{\infty} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} (\xi^2+\eta^2+\zeta^2)n^{(e)}{}_{\xi,\eta,\zeta}\, d\zeta = \frac{m\pi C}{2h^3}\left(1-\frac{3h'}{h}\right), \tag{24b}$$

so that

$$\frac{C\pi}{h^2}\left(1-\frac{3h'}{h}\right) = \frac{N}{\sqrt{\pi h}}\ (1+\tfrac{5}{4}\sqrt{\pi h}\ \mathfrak{a}\ V). \tag{24}$$

From (23) and (24) we obtain

$$\left.\begin{aligned} C &= \left(\frac{h}{\pi}\right)^{3/2} N(1+\tfrac{1}{2}\sqrt{\pi h}\,\mathfrak{a}V) \\ h' &= -\frac{\sqrt{\pi}}{4}\ h^{3/2}\,\mathfrak{a}\ V. \end{aligned}\right\} \tag{25}$$

Finally we have to compute the momentum carried away by the reflected molecules

$$-M_S^{(e)} = m\int_0^{\infty} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \xi n^{(e)}_{\xi,\eta,\zeta} d\zeta = \frac{mC}{4h}\left(\frac{\pi}{h}\right)^{3/2}\left(1-\tfrac{5}{2}\frac{h'}{h}\right) \tag{26}$$

or substituting the expressions (25) and putting, as before, $\alpha = \cos\theta$, $\sqrt{\pi h} = 2/\bar{c}$ and taking into account only the term dependent on V

$$M_S^{(e)} dS = -\tfrac{9\pi}{64} Nm\bar{c} V \cos\theta \, dS.$$

Integrating the projection of this on the direction of motion over the whole surface of the sphere, we get

$$M_{4a}^{(e)} = -\tfrac{3\pi^2}{16} Nm\bar{c}a^2 V$$

and

$$M_{4a} = M_{4a}^{(e)} + M^{(i)} = -(\tfrac{4}{3}+\tfrac{3\pi}{16})\pi Nm\bar{c}a^2 V. \tag{27}$$

Case (4b). The sphere is a perfect thermal conductor. In this case the energy balance need not be maintained for the individual surface elements and is obviously satisfied for the sphere as a whole if we assume that its temperature is everywhere the same as that of the gas. We have, therefore, to drop condition (24) and put $h' = 0$; then (23) gives

$$C = N\left(\frac{h}{\pi}\right)^{3/2}(1+\sqrt{\pi h} V\cos\theta). \tag{28}$$

Substituting this into (26)

$$M_S^{(e)} dS = -\tfrac{\pi}{8} Nm\bar{c} \; V\cos\theta \, dS$$

and integrating over the surface

$$M_{4b}^{(e)} = -\tfrac{\pi^2}{6} Nm\bar{c} \; a^2 V$$

and

$$M_{4b} = M_{4b}^{(e)} + M^{(i)} = -\tfrac{\pi}{3}\,(4+\tfrac{1}{2}\pi) Nm\bar{c}\, a^2 V. \tag{29}$$

7. *Millikan's coefficient* $(A+B)$. We can summarize the results of the two preceding sections in the following way. In all cases the force of resistance is given by the expression

$$F = -M = \delta \cdot \tfrac{4\pi}{3} Nm\bar{c}\, a^2 V, \tag{30}$$

where δ is a numerical factor having the following values:

Case (2). Specular reflection

$$\delta_2 = 1$$

Case (3). Diffuse reflection with conservation of velocity

$$\delta_3 = \tfrac{13}{9} = 1.444$$

Case (4). Diffuse reflection with accommodation containing the two subcases of section 6

$$\delta_{4a} = 1+\tfrac{9\pi}{64} = 1.442$$
$$\delta_{4b} = 1+\tfrac{\pi}{8} = 1.393$$

Millikan has shown that the experimental values for the force of resistance when the radius a is small compared with the mean free path l can be represented by the formula

$$F=\frac{6\pi a^2\mu V}{(A+B)l} \tag{31}$$

where μ is the coefficient of viscosity

$$\mu=0.3502\ Nm\bar{c}l. \tag{32}$$

Comparing expressions (30) and (31) we find

$$A+B=\frac{9\times 0.3502}{2\delta}=\frac{1.575}{\delta}.$$

Using the above values of δ we find for:

Case (2). *Specular reflection*

$$(A+B)_2=1.575$$

Case (3). *Conservation of velocity*

$$(A+B)_3=1.091$$

Case (4). *Accommodation*

$$(A+B)_{4a}=1.093$$
$$(A+B)_{4b}=1.131$$

The experiments of Millikan were made with oil drops, and by observing comparatively large drops he had previously ascertained that one tenth of the molecules followed the law of specular reflection. Let us, therefore, inquire about the force of resistance in the case when different fractions s of the impinging molecules are subject to different laws of reflection; obviously the expression for this force will be

$$F=\sum s\delta\cdot\tfrac{4\pi}{3}Nm\bar{c}\ a^2V$$

so that we obtain for Millikan's coefficient

$$A+B=\frac{1.575}{\sum s\delta} \tag{33}$$

We shall assume that one tenth of the molecules are reflected specularly, and that the rest all follow the same law (diffuse reflection or evaporation)

$$A+B=\frac{1.575}{0.1+0.9\delta}.$$

This gives us for the various cases

Case (3). *Conservation of velocity*

$$(A+B)_3=1.125$$

Case (4). *Accommodation*

$$(A+B)_{4a}=1.127$$
$$(A+B)_{4b}=1.164$$

The experimental value found by Millikan for oil drops is 1.154 (while Knudsen obtained for glass spheres 1.164) which is especially close to our theoretical value $(A+B)_{4b}$. However, the agreement with the values $(A+B)_3$ and $(A+B)_{4a}$ is also pretty satisfactory, so that it would be rash to regard this as convincing evidence in favor of the hypothesis that the sphere can be regarded as a perfect conductor. Fortunately we can decide the question by other considerations. The behavior of the sphere depends on the ratio of the heat transported through its interior, which we may call the *internal conduction*, to the heat received in unit time from the molecular impacts, *external conduction*. If the increase of temperature of a surface element is ΔT, the internal conduction, obviously will be of the order of magnitude

$$C^{(i)}=\frac{\kappa\Delta T}{a}$$

κ being the coefficient of conductivity of the material and a the radius. In the most favorable case the increase of the constant $h=m/2kT$ is according to the formulas (25) given by

$$h'=\Delta h=-\frac{m}{2kT^2}\Delta T=-\frac{\sqrt{\pi}}{4}h^{3/2}aV,$$

whence

$$\Delta T=\tfrac{1}{4}\frac{\sqrt{\pi mT}}{2k}\cdot aV$$

and

$$C^{(i)}=\frac{\kappa}{4a}\frac{\sqrt{\pi mT}}{2k}\cdot aV.$$

With $\kappa=1.65\cdot10^{4}$ (olive oil), $m=4.5\cdot10^{-23}$(air), $k=1.33\cdot10^{-1}$, $T=300°$,

$$C^{(i)}=\frac{209}{4a}aV.$$

On the other hand the external conduction in the most favorable case can be derived from equations (24a), (24b) and (28) by putting $h'=0$

$$C^{(e)}=\tfrac{1}{4}\frac{mN}{2h}aV.$$

The factor $mN/2h$ is just equal to the pressure of the gas p and this pressure is inversely proportional to the mean free path: $p/p_0=l_0/l$; Since for a pressure of 1 atmosphere p_0 is close to 10^6 c.g.s. units, $l_0=5.9\cdot10^{-6}$ cm, we get $p=5.9/l$ and

$$C^{(e)}=\frac{5.9}{4l}aV.$$

The ratio of the internal conduction to the external is, therefore,

$$\frac{C^{(i)}}{C^{(e)}} = 35\frac{l}{a}. \tag{34}$$

If the accommodation is incomplete the factor 35 must be increased in the ratio $1/\sigma$.

We see from this that if $l/a << 1/35$, the internal conduction can be neglected and the oil drop will behave like a perfect insulating sphere. On the other hand, if $l/a >> 1/35$, the oil drop can be regarded as a perfectly conducting sphere. The considerations of the first part of our paper apply to large values of l/a; in fact Millikan derived the aforesaid value of $A+B$ from measurements with values of this ratio as high as 140 which is five thousand times larger than our critical number 1/35. It follows that only the hypothesis underlying the result $(A+B)_{ab}$ is justified, so that *the agreement between theory and experiment is complete.*

If we turn to the opposite case of comparatively large spheres, to which the second part of this paper is devoted, we meet quite different conditions; the actual measurements[1] of the coefficients A were made with values of the ratio l/a not far from our critical value 1/35. This, however, does not imply any difficulty for the theory, as in the case of large spheres it happens that $\Delta T = O$. Under no circumstances does there occur a local increase in temperature so that the two cases of this section need not be discriminated there.

Part II. Resistance Experienced by Comparatively Large Spheres

8. *Conditions to which the gas is subject.* The difference between the case of large spheres and that of small spheres treated in the first part is that the sphere exercises an important influence on the whole character of motion of the gas molecules. The distribution of velocities in the gas will no longer follow the Maxwell law of Eq. (1), but will have a quite different expression which we now propose to find. This problem has been already treated by Maxwell, but in the special case when temperature differences do not exist in the gas, the solution can be found in a very simple way by a method used by the author several years ago in considerations referring to space charge phenomena.[7] This method has the advantage that it is based on the principle of Boltzmann and is free from any assumptions further than those which his principle implies as to the

[7] P. S. Epstein, Verh. der deutsch. Phys. Ges. **21**, 96, 1919. The same method was applied to the theory of the radiometer by Miss E. Einstein in a recent investigation (Ann. der Phys. **69**, 241, 1922) which was begun under the supervision of the writer.

mechanism of the molecular collisions, while Maxwell's considerations were restricted to molecules behaving like perfectly elastic spheres.

The hydrodynamical expression for the fact that the conditions of motion of the gas are changed by the presence of the sphere consists in the appearance of a system of hydrodynamical stresses, dependent on the velocities. If we denote by u, v w the components of the (macroscopic) velocity of the gas in the directions x, y, z, the stress components are

$$\left.\begin{aligned} &p_{xx}=-p+2\mu\frac{\delta u}{\delta x}, \quad p_{yy}=-p+2\mu\frac{\delta v}{\delta y}, \quad p_{zz}=-p+2\mu\frac{\delta w}{\delta z}, \\ &p_{yz}=\mu\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right), \quad p_{zx}=\mu\left(\frac{\delta u}{\delta z}+\frac{dw}{\delta y}\right), \quad p_{xy}=\mu\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right). \end{aligned}\right\} \tag{35}$$

If we return to the kinetic point of view, we must say that all the macroscopic characteristics of the gas are a result of the co-operation of the individual molecules. Let the number of molecules have velocities between ξ, η, ζ and $\xi+d\xi, \eta+dy, \zeta+d\zeta$ at some point of the gas be given by

$$f(\xi, \eta, \zeta)d\xi d\eta d\zeta = f d\omega. \tag{36}$$

Then the density of the gas at this point will be

$$\rho = m\int f d\omega. \tag{37a}$$

The mass flowing across a unit of area in the respective directions x, y, z, will be

$$\rho u = m\int \xi f d\omega, \quad \rho v = m\int \eta f d\omega, \quad \rho w = m\int \zeta f d\omega. \tag{37b}$$

Finally, the physical meaning of the stress components (35) is the transportation of a given component of momentum in a given direction:

$$\left.\begin{aligned} &p_{xx}=-m\int \xi^2 f d\omega, \quad p_{yy}=-m\int \eta^2 f d\omega, \quad p_{zz}=-m\int \zeta^2 f d\omega, \\ &p_{yz}=-m\int \eta\zeta f d\omega, \quad p_{zx}=-m\int \zeta\xi f d\omega, \quad p_{xy}=-m\int \xi\eta f d\omega. \end{aligned}\right\} \tag{37c}$$

Whatever the expression of f may be, it must be chosen so as to satisfy these ten conditions.

9. *Law of distribution of velocities.* The principles of statistical mechanics tell us that the correct law of distribution is that of the highest probability, or stated mathematically, according to Boltzmann's H-theorem, that for which

$$H=\int f \log f \, d\omega = \text{minimum}. \tag{38}$$

The special conditions by which the choice of f is restricted, of course, must be taken into account, and these are in our case the ten conditions (37*a*, *b*, *c*). The problem is, therefore, reduced to that of finding the minimum of a function subject to additional conditions, and the rule for this is, as is well known, to multiply the relations (37*a*, *b*, *c*) by Lagrangian factors, to add them to H, and to put the variation of the sum

equal to zero. Denoting the factors by $-(\log P+1)$, a', b', c', l', m', n', $2p'$, $2q'$, $2r'$, respectively, we arrive at the equation

$$\delta\int f\cdot[\log f-(\log P+1)+a'\xi+b'\eta+c'\zeta+l'\xi^2+m'\eta^2+n'\zeta^2+ \\ +2p'\eta\zeta+2q'\zeta\xi+2r'\xi\eta]d\omega=0$$

or

$$\log f=\log P-(a'\xi+b'\eta+c'\zeta)-(l'\xi^2+m'\eta^2+n'\zeta^2+ \\ +2p'\eta\zeta+2q'\zeta\xi+2r'\xi\eta). \tag{39}$$

In the applications we shall restrict ourselves to the case in which the function f differs very little from that of the law of Maxwell

$$f_0=N\left(\frac{h}{\pi}\right)^{3/2}e^{-h(\xi^2+\eta^2+\zeta^2)} \tag{40}$$

so that we can put

$$l'=h+l'', \quad m'=h+m'', \quad n'=h+n'' \tag{41}$$

where l'', m'', n'', as well as a', b', c', p', q', r' are very small quantities the squares of which may be neglected. We get, therefore,

$$f=Pe^{-h\zeta^2}\{1-(a'\xi+b'\eta+c'\zeta)-(l''\xi^2+m''\eta^2+n''\xi^2+ \\ +2p'\eta\zeta+2q'\zeta\xi+2r'\xi\eta)\}. \tag{42}$$

It only remains to calculate the ten constants of this expression from the ten equations (37*a*, *b*, *c*). If we denote

$$P=\left(\frac{h}{\pi}\right)^{3/2}N_0=\left(\frac{h}{\pi}\right)^{3/2}\frac{\rho_0}{m} \tag{43}$$

the first of those conditions gives us

$$\rho=\rho_0[1-\frac{1}{2h}(l''+m''+n'')]$$

and

$$\rho_0=\rho[1+\frac{1}{2h}(l''+m''+n'')] \tag{44a}$$

The equations (37b)

$$u=-\frac{a'}{2h}, \qquad v=-\frac{b'}{2h}, \qquad w=-\frac{c'}{2h}, \tag{44b}$$

and equations (37c) combined with (44a)

$$p_{xx}=-\frac{\rho}{2h}\left(1-\frac{l''}{h}\right), \quad p_{yy}=-\frac{\rho}{2h}\left(1-\frac{m''}{h}\right), \quad p_{zz}=-\frac{\rho}{2h}\left(1-\frac{n''}{h}\right),$$

$$p_{yz}=-\frac{\rho}{2h^2}p', \qquad p_{zx}=-\frac{\rho}{2h^2}q', \qquad p_{xy}=-\frac{\rho}{2h^2}r'. \tag{44c}$$

Taking into account that

$$\frac{\rho}{2h}=p \tag{45}$$

and denoting

$$p'_{xx}=2\mu\frac{\delta u}{\delta x},\qquad p'_{yy}=2\mu\frac{\delta v}{\delta x},\qquad p'_{zz}=2\mu\frac{\delta w}{\delta z} \tag{46}$$

we finally obtain

$$\begin{cases} a'=-2hu, & b'=-2hv, & c'=-2hw,\\ l''=\dfrac{2h^2}{\rho^2}p'_{xz}, & m''=\dfrac{2h^2}{\rho}p'_{yy}, & n''=\dfrac{2h^2}{\rho}p'_{zz},\\ p'=\dfrac{2h^2}{\rho}p_{yz}, & q'=\dfrac{2h^2}{\rho}p_{zz}, & r'=\dfrac{2h^2}{\rho}p_{xy}. \end{cases}$$

The sum

$$l''+m''+n''=4h^2\frac{\mu}{\rho}\left(\frac{\delta u}{\delta x}+\frac{\delta v}{\delta y}+\frac{\delta w}{\delta z}\right)$$

can on account of the equation of continuity

$$\frac{\delta(\rho u)}{\delta x}+\frac{\delta(\rho v)}{\delta y}+\frac{\delta(\rho w)}{\delta z}=0$$

differ from zero only by terms of the second order in the velocities, which we have consistently neglected. Practically, therefore, $\rho_0=\rho$ and the distribution function now acquires the form

$$f=f_0[1-2h(u\xi+v\eta+w\zeta)+\frac{2h^2}{\rho}\ (p'_{xx}\,\xi^2+p'_{yy}\,\eta^2+ \\ +p'_{zz}\,\zeta^2+2p_{yz}\,\eta\zeta+2p_{zz}\,\zeta\xi+2p_{xy}\,\xi\eta)]. \tag{47}$$

10. *Conditions at the surface of an immersed body.* The distribution function found in the preceding section is strictly valid only for interior points of the gas. Close to its boundary it necessarily must be changed, due to the fact that, near the surface of an immersed body, the molecules having a positive ξ component of velocity (as before we choose the normal direction as the x-axis) are those which come from the surface after being reflected from it. As the total force acting on some volume of the gas is equal to the transportation of momentum through the surface of this volume, it is obvious that the transportation of momentum or, in other words, the stress tensor is the quantity which regulates the equilibrium of the gas. A stationary state is only then reached when the reflected portion of the molecules no longer disagrees with the conditions prevailing at the interior points of the medium, but fits into the system of stresses given by equations (37*c*). In other words, the reflected molecules must produce the same effects, as to the transportation of momentum, which molecules moving with a positive ξ component and the velocity distribution $f(\xi, \eta, \zeta)$ of the preceding section would produce in the absence of a boundary.

The number of molecules of the range of velocities between ξ, η, ζ and $\xi+d\xi, \eta+d\eta, \zeta+d\zeta$ which impinge on a surface element dS in unit time is, as stated in section 3, $-\xi f(\xi, \eta, \zeta)d\xi\, d\eta\, d\zeta\, dS$, provided that ξ is negative. Let the fraction $(1-s)$ of this number undergo specular reflection, and the fraction s diffuse reflection, in which latter case the law of distribution of velocities among the emerging molecules will be a new one, given by the expression $f'(\xi, \eta, \zeta)$. According to the above remarks the totality of all reflected molecules must carry exactly the same momentum that would be carried by molecules having the distribution $f(\xi, \eta, \zeta)$ and a positive ξ component, so that the stresses produced by the former and the latter are the same. This gives us at once six conditions for the six stress components. The first of them is

$$s\int_0^\infty d\xi\int_{-\infty}^{+\infty} d\eta\int_{-\infty}^{+\infty}\xi^2 f'(\xi,\eta,\zeta)d\zeta+(1-s)\int_{-\infty}^{0} d\xi\int_{-\infty}^{+\infty} d\eta\int_{-\infty}^{+\infty}\xi^2 f(\xi,\eta,\zeta)d\zeta=$$

$$=\int_0^\infty d\xi\int_{-\infty}^{+\infty} d\eta\int_{-\infty}^{+\infty}\xi^2 f(\xi,\eta,\zeta)d\zeta.$$

By choosing in the second integral as the variable of integration $-\xi$ instead of ξ, we can reduce this to the form

$$\int_0^\infty d\xi\int_{-\infty}^{+\infty} d\eta\int_{-\infty}^{+\infty}\{sf'(\xi,\eta,\zeta)+(1-s)f(-\xi,\eta,\zeta)-f(\xi,\eta,\zeta)\}\xi^2 d\zeta=0. \qquad (48a)$$

In a similar way we get for the normal stress in the y-direction

$$\int_0^\infty d\xi\int_{-\infty}^{+\infty} d\eta\int_{-\infty}^{+\infty}\{sf'(\xi,\eta,\zeta)+(1-s)f(-\xi,\eta,\zeta)-f(\xi,\eta,\zeta)\}\eta^2 d\zeta=0, \qquad (48b)$$

and a third similar equation for the z-component.

Turning to the shearing stresses we have to take into account that $f'(\xi,\eta,\zeta)$ represents a distribution symmetrical with respect to the normal. Therefore the diffusely reflected molecules cannot produce any shearing stresses and the term of the equation depending on f' must vanish. We have, therefore,

$$\left.\begin{aligned}\int_0^\infty d\xi\int_{-\infty}^{+\infty} d\eta\int_{-\infty}^{+\infty}\{(1-s)f(-\xi,\eta,\zeta)-f(\xi,\eta,\zeta)\}\xi\eta\, d\zeta=0,\\ \int_0^\infty d\xi\int_{-\infty}^{+\infty} d\eta\int_{-\infty}^{+\infty}\{(1-s)f(-\xi,\eta,\zeta)-f(\xi,\eta,\zeta)\}\xi\zeta\, d\zeta=0,\end{aligned}\right\} \qquad (49)$$

and a third relation which is satisfied identically.

To these five conditions two more must be added, expressing the principle of conservation of mass and that of conservation of energy. The

number of molecules impinging on a surface element of the boundary is equal to the number reflected from it, and the energy brought by the first group of molecules to this element is equal to that carried away by the second. As these demands are obviously satisfied by the part of the molecules undergoing specular reflection, we need to state it only for those reflected diffusely. We have, therefore,

$$\int_0^\infty d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \{f'(\xi,\eta,\zeta) - f(-\xi,\eta,\zeta)\}\,\xi\, d\zeta = 0, \tag{50}$$

$$\int_0^\infty d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \{f'(\xi,\eta,\zeta) - f(-\xi,\eta,\zeta)\}\,\xi(\xi^2+\eta^2+\zeta^2) d\zeta = 0. \tag{51}$$

The seven conditions of this section must be satisfied by a suitable choice of the coefficients u, v, w, p_{xx}, etc. of the function f and of those of the function f'. Of the former, according to equations (35), only three are arbitrary.

11. *Conclusions drawn from the kinetic boundary conditions.* Into the equations of the last section we have to introduce for f' the function representing the velocity distribution of molecules reflected diffusely with accommodation. According to section 6 the law can be written in the form

$$f' = f_0\{1 + P' - h'(\xi^2+\eta^2+\zeta^2)\}. \tag{52}$$

If we limit our considerations to the case of surfaces with comparatively large radii of curvature R_1 so that the ratio of the mean free path of the gas l to R becomes so small that the square of l/R can be neglected (as well as the products of the velocities u, v, w, with l/R), then the form of the distribution function f can be simplified.

Indeed, if we have no slip at the surface, the velocity components close to it must vanish; $u = v = w = 0$, whence at the surface

$$\frac{\delta u}{\delta x} = \frac{\delta v}{\delta y} = \frac{\delta w}{\delta z} = 0.$$

If there exists a slip, the velocity at the surface can only be of the order of magnitude vl/R, while p'_{xx}, p'_{yy}, p'_{zz}, due to the differentiation and to the factor μ are still a second time multiplied by l/R. Therefore, within the limits of the accuracy of our theory we can put, compared with p_{yz} etc.,

$$p'_{xx} = p'_{yy} = p'_{zz} = 0 \tag{53}$$

so that close to the boundary the function f assumes the form

$$f = f_0\left\{1 - 2h(u\xi + v\eta + w\zeta) + \frac{4h^2}{\rho}(p_{yz}\eta\zeta + p_{zx}\zeta\xi + p_{xy}\xi\eta)\right\}. \tag{54}$$

We introduce this formula into the two conditions (49) of the last section independent of f' and obtain

$$\left.\begin{aligned} v &= \frac{\sqrt{\pi h}}{\rho}\left(\frac{2}{s}-1\right)p_{xy}, \\ w &= \frac{\sqrt{\pi h}}{\rho}\left(\frac{2}{s}-1\right)p_{xz}. \end{aligned}\right\} \tag{55}$$

The three conditions (48) yield all one and the same relation

$$(2-s)u+\tfrac{1}{4}\sqrt{\frac{\pi}{h}}\,P'-\frac{5}{8}\sqrt{\frac{\pi}{h}}\,\frac{h'}{h}=0.$$

From (50) we obtain

$$u-\frac{1}{\sqrt{\pi h}}\,P'+\frac{12}{\sqrt{\pi h}}\,\frac{h'}{h}=0,$$

and from (51)

$$5u-\frac{1}{\sqrt{\pi h}}\,P'+\frac{12}{\sqrt{\pi h}}\,\frac{h'}{h}=0.$$

The solution of these equations is

$$P'=0, \quad h'=0, \tag{56}$$

$$u=0. \tag{57}$$

The result (56) shows us that the velocity distribution among the diffusely reflected molecules is the plain Maxwell distribution, corresponding to the temperature and density of the surrounding gas. There is no local heating of the immersed body, as we already mentioned in section 6. It is interesting to point out that the assumption of the conservation of velocity would lead to exactly the same result, so that the case of a large sphere does not permit us to differentiate between the two possibilities. The analysis of the motion of small spheres is in this respect superior to the case here considered.

Equation (57) together with (55) gives us the macroscopic boundary conditions necessary for the solution of the hydrodynamical problem. We see that they formally coincide with the phenomenological assumptions introduced by Basset:

$$\left.\begin{aligned} u &= 0, \\ p_{xy} &= \beta v, \\ p_{xz} &= \beta w. \end{aligned}\right\} \tag{58}$$

β is called the "coefficient of sliding friction" and μ/β the "slip coefficient." Comparing (55) with (58) and taking into account relations (12) and (32), we get as expression of the slip coefficient

$$\frac{\mu}{\beta}=0.7004\left(\frac{2}{s}-1\right)l, \tag{59}$$

in agreement with Maxwell's value, so that the conditions at a surface of sufficiently small curvature are, with respect to sliding, the same as at a plane surface.

It must, however, be remarked that though equations (55), (57) and (58) are formally identical, v and w in (55) are not the actual velocity components at the surface but those values which the components would have if the distribution function f and the hydrodynamical equations were rigorously valid up to the immediate vicinity of the boundary. As the solution of the latter equations in the case of a sphere can be found in most text-books of hydrodynamics, it is not necessary to repeat it here. The force of resistance experienced by a sphere, or, according to Eqs. (37c), the momentum conferred on the sphere by the gas molecules in unit time, is given by Basset's formula,[8]

$$M = -6\pi\mu a V \cdot \frac{2\mu+\beta a}{3\mu+\beta a}. \tag{60}$$

It must be borne in mind, however, that we have found the assumptions (58), underlying Basset's formula, to be valid only in the case when squares of the ratio l/a can be neglected, so that it would be more consistent to neglect such terms in the expression of the resistance itself and to write the formula in the form

$$M = -6\pi\mu a V\left(1-\frac{\mu}{\beta a}\right) = -\frac{6\pi\mu a V}{1+\frac{\mu}{\beta a}}. \tag{61}$$

This can be hardly regarded as a limitation, because, if l/a is not small, the applicability of hydrodynamics begins anyway to break down.

As we have obtained a complete confirmation of the two formulas (61) and (59) on which Millikan's theory is based, all his conclusions, especially as to the percentage of specular reflection, seem unimpeachable.

12. APPENDIX. On the Rotational Motion of Spheres

At the Boston meeting of the American Physical Society, where an abstract of this paper was read, my attention was drawn by Dr. G. Breit to the importance which the knowledge of the resistance experienced by a sphere rotating in a gaseous medium presents. Dr. Breit is going to publish in this connection some interesting considerations of his own, but I should like to point out here what our general formulas yield for this special case.

As in the case of a translatory motion we have to distinguish between the two cases when the radius of the sphere is small compared with the mean free path and when it is large compared with it.

[8] Basset, Hydrodynamics, **2**, 271; H. Lamb, Hydrodynamics (4th ed.), p. 591

Case 1. $a << l$. We choose, as in section 3, the normal to the surface as the x-direction, the meridian through the axis of rotation as the y-axis, and the parallel circle in the direction of rotation as the z-axis. As every surface element moves in its own plane in the direction z, we have to specialize the angles in formula (13) as follows:

$$\alpha = 0, \quad \beta = 0, \quad \gamma = 1.$$

We wish, moreover, to compute the component of the momentum communicated by the gas to a surface element dS in the direction of its motion, so that

$$\alpha' = 0, \quad \beta' = 0, \quad \gamma' = 1.$$

The aforesaid momentum, therefore, turns out to be

$$M_S^{(i)} dS = -\tfrac{1}{4} N m \bar{c} V dS \tag{62}$$

From this it is easy to obtain the moment of momentum Y, with respect to the axis of rotation, acquired by the surface element in unit time; it suffices to multiply this expression by the distance from the axis. Taking the center of the sphere as origin of a system of polar coordinates r, θ, φ and the axis of rotation as the polar axis, we get for that distance $a \sin\theta$, while $dS = a^2 \sin\theta \, d\theta \, d\varphi$ and $V = a\omega \sin\theta$. Hence if we denote the angular velocity of rotation by ω,

$$Y_S^{(i)} dS = -\tfrac{1}{4} N m \bar{c} \omega a^4 \sin^3\theta d\theta d\varphi.$$

The total moment of momentum conferred to the sphere by the impinging molecules is obtained by integrating over the whole surface of the sphere and comes out

$$Y^{(i)} = -\tfrac{2\pi}{3} N m \bar{c} \omega a^4. \tag{63}$$

As to the momentum of the reflected molecules, it is evident that the effect of the specularly reflected will just cancel that of the corresponding impinging ones; while the diffusely reflected emerge symmetrically with respect to the normal, and yield, therefore, no contribution to the moment of momentum. If we denote the fraction of the molecules undergoing diffuse reflection by s, the total resistance will be

$$Y = -\tfrac{2\pi}{3} s \, N m \bar{c} \omega a^4, \tag{64}$$

or, according to equation (32)

$$Y = -2.185 \pi s \mu \omega a^3 \frac{a}{l}. \tag{64'}$$

If the measurement of resistance under the above conditions is experimentally feasible, it will yield a direct determination of the fraction s of diffusely reflected molecules.

Case 2. $a >> l$. According to section 11, we have to solve in this case the problem of the motion of a viscous fluid with the boundary condi-

tions (58). The general solution in the case when the square of the velocity is negligible, can be found in most text-books of hydrodynamics;[9] the velocity V of the liquid or gas turns out to have in the direction of the above polar coordinates the components:

$$V_r=0, \quad V_\theta=0, \quad V_\varphi=\frac{C}{r^2}\sin\theta.$$

From this we get the stress components at the surface of the sphere in our previous notations (taking again the z-axis in the direction of the parallel circle)

$$p'_{xx}=p'_{yy}=p'_{zz}=0,$$
$$p_{yz}=p_{zx}=0, \quad p_{xy}=-3\mu\frac{C}{a^3}\sin\theta. \tag{65}$$

In giving the values of u, v, w it must be taken into account that in (58) they are the components of the *relative* velocity of the gas with respect to the surface of the sphere. Therefore:

$$u=0, \quad v=\left(\frac{C}{a^2}-a\omega\right)\sin\theta, \quad w=0. \tag{66}$$

Of the three conditions (58) two are satisfied identically, the third gives an equation for the determination of the constant C:

$$\beta\left(\frac{C}{a^2}-a\omega\right)=-3\mu\frac{C}{a^3},$$

whence

$$C=\frac{a^3\omega}{1+\frac{3\mu}{\beta a}}=\frac{a^3\omega}{1+2.1012\left(\frac{2}{s}-1\right)\frac{l}{a}}.$$

We obtain the resistance by integration of the moment $p_{zy}\cdot a\sin\theta\, dS$, acting on a surface element, over the whole surface

$$Y=-8\pi\mu C=-\frac{8\pi\mu a^3\omega}{1+2.1012\left(\frac{2}{s}-1\right)\frac{l}{a}}. \tag{67}$$

We see that the correction due to the finite value of the mean free path is three times as large in the case of the translatory motion of a sphere.

In certain theories of dispersion the rotation of molecules plays a conspicuous part and the resistance offered by the medium of this rotation is computed as if the molecules were spheres on the basis of the uncorrected equation

$$Y=-8\pi\mu a^3\omega. \tag{68}$$

In reality, the application of any theory becomes doubtful under those conditions. Even if it is permissible to regard a molecule as a sphere, the radius and the mean free path are of the same order of magnitude, so

[9] H. Lamb, Hydrodynamics (4th ed.), p. 581

that neither formula (64) and (67) is applicable. There is, however, little doubt that the true resistance for $l=a$ must be smaller than that given by either of the two expressions, and is therefore, more than three times smaller than that derived from formula (68).

Another cause of uncertainty is the deviation of the molecules from a spherical shape. It is interesting in this connection to compute what the resistance of a flat disk of the radius a will be, revolving with constant angular velocity around an axis in its plane passing through its center. The computation is easy on the basis of our general results in the case $a<<l$. Assuming that a fraction $(1-s)$ of the molecules is reflected specularly and a fraction s undergoes diffuse reflection with accommodation (section 6) and that the disk acts like a perfect conductor, we get the expression

$$Y=-\tfrac{1}{4}\pi N m\bar{c}a^4[2-s+\tfrac{1}{4}\pi s]\cdot\omega. \tag{69}$$

If the percentage of specular reflection is fairly low the difference between this case and that of formula (64) is not very important. From all these considerations we can draw the conclusion that formula (68) will give us only the rough order of magnitude of the resistance experienced by a rotating molecule, and its application is only justified when nothing but a rough estimate is required.

NORMAN BRIDGE LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
February 3, 1923.

STUDIES WITH IONIZATION GAUGE

C. G. FOUND AND S. DUSHMAN

II. RELATION BETWEEN IONIZATION CURRENT AT CONSTANT PRESSURE AND NUMBER OF ELECTRONS PER MOLECULE

ABSTRACT

Calibration constants for the ionization gauge in various gases.—The relation for the pressure $P = K \times$ positive ionization, where K is a constant, was found to hold for Hg vapor (.025 to .21 bar) and for iodine vapor assuming published values of vapor pressures. For H_2, He, Ne, N_2 and CO at pressures around 50 bars, readings were compared with those of a McLeod gauge and the values of K determined. For the same electrical conditions (anode voltage and electron current) $1/K$ is found to be proportional to the total number of electrons per molecule or molar number N, (except for H_2 and He for which KN is half as large). Measuring i_+ in microamps and P in bars, the value of the constant KN is 10.4 for an electron current at 0.5 m-amp. and an accelerating voltage of 125 volts. Results for the vapor pressure of water and of HgI_2 also agree with this relation.

Relative ionization due to slow electrons in various gases is, then,p roportional to the pressure and to the molar number (except for H_2 and He). This agrees with results previously obtained for ionization by α and β rays, except that for these H_2 is not abnormal. From the electron current, K and the mean free path, the fraction of the collisions with molecules which produce positive ions can be computed. It comes out ¼ in argon for an accelerating potential of 125 volts.

Vapor pressures of napthalene, —11° to 18°C, and of vacuum oil 0° and 25°C were determined, assuming probable values of K.

IN a previous paper[1] the authors have described the construction of an ionization gauge and a method of calibration using argon. The present paper deals with the calibration of the gauge with other gases and vapors and the relation that these calibrations bear to each other.

METHOD OF CALIBRATION WITH MERCURY VAPOR

The calibration of the ionization gauge for a vapor was made by comparing the gauge reading with the known vapor pressures at different temperatures. The arrangement of the apparatus used in the case of mercury is shown in Fig. 1. The ionization gauge was connected through two traps T_1 and T_2 to an exhaust system at P. The exhaust system consisted of a Langmuir condensation pump in series with an oil pump which was backed up by a rough vacuum line. A side tube S containing mercury was attached to the tube T_1. The gauge and trap T_1 were baked

[1] Dushman and Found, Phys. Rev., **17**, 7, (1921)

out in an oven at 360°C for an hour at the beginning of the exhaust. The tube S containing the mercury extended below the bottom of the oven and was heated gently by a Bunsen flame during the oven bake-out, in order to drive out all moisture and occluded gases. When the apparatus had cooled down after the oven bake-out, the tube S was immersed in liquid air and the metal parts of the gauge were bombarded as described in the previous paper. The liquid air was then transferred from S to the trap T_1 and the mercury distilled from the former to the latter, after which S was sealed off at C. The gauge was now connected with

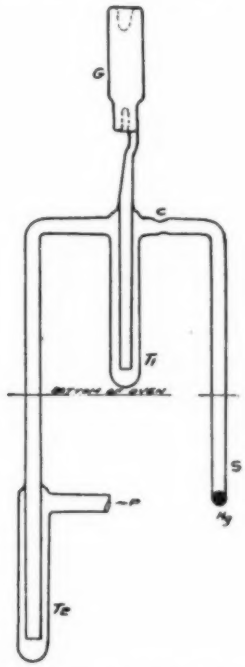

Fig. 1. Apparatus for calibration of ionization gauge with mercury vapor

the inner spiral as cathode, the outer spiral anode (at a positive potential of 250 volts), and the cylinder was made the collecting electrode with a negative potential of 22 volts relative to the negative end of the cathode.

With an electron current of 20 milliamperes to the anode the measurements of the positive ionization current showed that the pressure when the mercury vapor was condensed by liquid air, was less than .001 bar. The liquid air on T_1 was now replaced by a freezing mixture. The temperature of the mixture was measured and the ionization current was measured at definite intervals of time. These readings showed a gradual change in the amount of ionization which finally reached a

steady value. This value is a measure of the ionization in mercury at the pressure corresponding to the temperature of the freezing mixture.

By varying the temperature of the freezing mixture a series of ionization current readings corresponding to different temperatures were obtained. Since the ionization gauge was attached to the inner part of the trap T_1, the pressure of mercury vapor in G was the pressure corresponding to the temperature of the freezing mixture.

While the measurements were being taken the exhaust system was connected to the gauge. This took out any reaction products which might be produced by the action of the hot cathode on the vapor, and also took care of residual gases which might happen to be liberated.

Table I gives the results obtained for mercury vapor. The pressures were extrapolated from data and from an extrapolation formula given in Kaye and Laby's Tables.

TABLE I

Readings in mercury vapor

Temperature of mixture	Pressure of mercury p	Positive ionization i	$K=P/i$
°C	.21 bar	57 (10)$^{-6}$ amp.	.0037
− 4	.13	38.5	.0034
− 8	.095	23.5	.0040
−10.9	.061	17.8	.0034
−12.7	.052	13.2	.0039
−13.9	.045	11.6	.0039
−16.7	.033	7.3	.0045
−18.9	.025	6.2	.0040
		Average value of $K=$	.0038

A plot of these results is shown in Fig. 2. From the slope of the line it is found that $K=.0038$.

MEASUREMENTS WITH OTHER GASES

The value of K obtained for argon[1] with the same electrical connection was .0132. Such a large variation in the relative ionization for the two gases suggested measurements with other gases.

It was shown in the previous paper[1] that the linear relation ($P=Ki$) between pressure and ionization current is valid up to pressures as high as 50 bars when the electron current is reduced to 0.5 milliamperes and the anode voltage to 125 volts. By working under these conditions, we were able to compare the ionization gauge readings for non-condensible gases, with pressures measured by a McLeod gauge. The use of these relatively higher pressures also reduced the effect of any impurity which might come from the glass walls, although precautions were taken to reduce this as much as possible. The ionization gauge was baked out

in an oven at 360°C for one hour and was washed out several times with the gas to be used before the measurements were taken. The ionization currents were then measured for different pressures.

Measurements were made with iodine using an arrangement similar to that employed for mercury. The vapor pressure data were taken from the published results of Haber and Kirschbaum.[2]

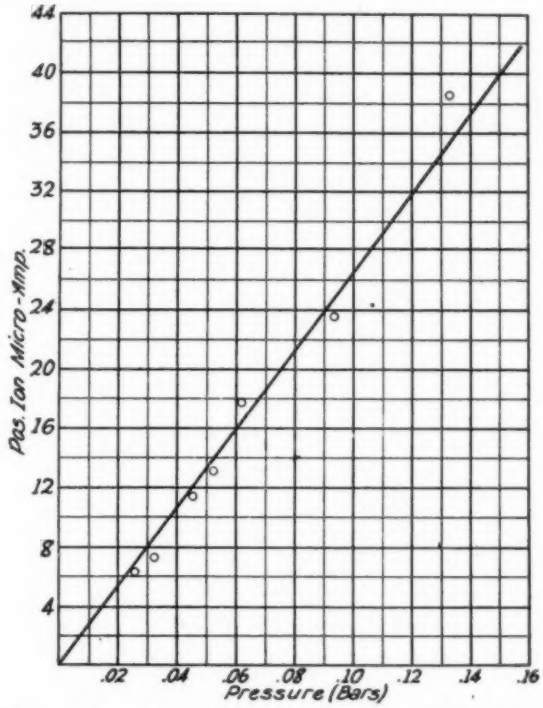

Fig. 2. Calibration of ionization gauge with mercury vapor. Anode voltage 250; collector voltage −22; current 22 milli-amp.

Table II gives the results obtained for the different gases.

TABLE II

Results for various gases

Gas	$K=P/i$	$1/K$	N	KN
Helium	2.74	.36	2	5.5
Neon	1.08	.92	10	10.8*
Argon	.58	1.72	18	10.6
Nitrogen	.67	1.51	14	9.4
Carbon monoxide	.72	1.39	14	10.1
Mercury	.13	7.6	80	10.5
Iodine	.10	9.8	106	10.6

[2] Haber and Kirschbaum, Zeit. f. Elektrochem. **20**, 296 (1914)

* We are indebted to Dr. K. H. Kingdon for the measurements with neon.

The variation in the value of K shown in the second column of the above table suggested that this constant is connected with the molecular structure of the gas.

In Fig. 3 we have plotted the values of $1/K$ against the number of electrons per molecule (this will be called molar number). It will be observed that, at constant electron current, the ionization per bar is proportional to the molar number. While this relation has not been subjected to extremely accurate measurements, the present results show that

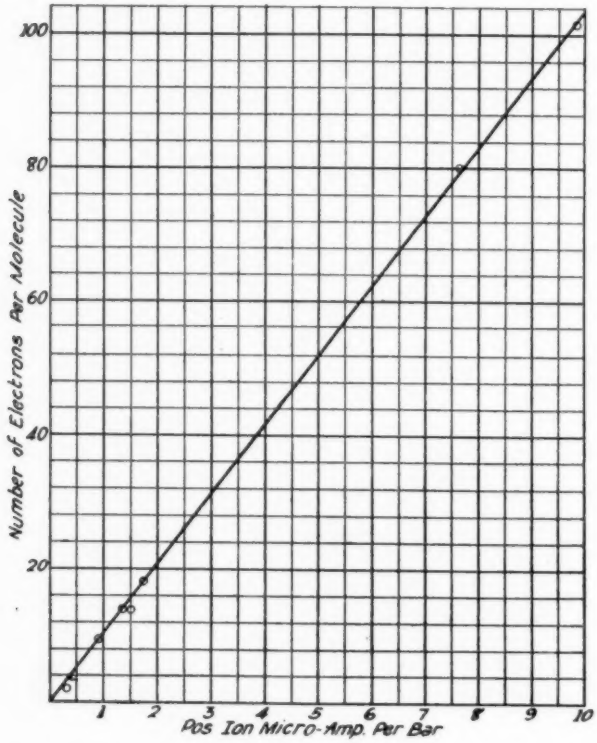

Fig. 3. Variation of the relative ionization of low velocity electrons with the number of electrons per molecule.
Anode voltage 125; collector voltage 22; current 0.5 milli-amp.

this is at least approximately true for the gases mentioned in Table II and is valid over a range from $N=10$ to $N=106$. The last column of Table II gives the product KN, which is approximately constant.

It will be observed that the values of K for argon and mercury as obtained with an electron current of 20 milliamperes are 0.0132 and 0.0038 respectively while the values obtained with 0.5 milliampere are 0.58 and 0.13 respectively. The ratio of the values of K is 3.5 in the first

case and 4.4 in the latter. Since the measurements with 0.5 milliampere were carried out at higher pressures, the ratio 4.4 has been considered as much more reliable. However, it is also essential to point out that owing to traces of other gases and other conditions under which the observations were taken, the accuracy of the values of K given in Table II is probably not greater than 10 per cent. This would account for the difference between the values obtained for nitrogen and carbon monoxide which, if the conclusion reached in the present investigation is valid, ought to be identical.

While the actual values of K were found to vary with the anode voltages such variations were only slight when voltages over 250 were used with 20 milliampere electron current, and for voltages over 125 with 0.5 milliampere. Furthermore the relative values of K for different gases were found to vary only slightly with varying anode voltages.

Hydrogen and helium both show consistently higher values of ionization than would be expected from the above relation between ionization and molar number. Measurements with these gases are extremely difficult since small amounts of other gases affect the ionization to a relatively greater extent, although in the present case extreme precautions were taken to eliminate impurities as much as possible. Moreover, in the case of hydrogen it is difficult to maintain constant pressure on account of the rapid cleanup by the hot cathode. However, all the results are consistent in indicating much smaller values of KN. This is in agreement with results of other observers. Kossel[3] found that the total ionization was proportional to the molecular weight for electrons having velocities equivalent to 100 volts except in the case of hydrogen which gave double that expected from density relation. Lenard[4] and Strutt[5] obtained the same results for cathode rays and β rays respectively.

Ionization by Other Means

Kleeman[6] has summarized the work on relative ionization for α, β and x-rays. The results obtained by him for the ionization by α and β rays are analogous to those obtained in the present investigations, i. e., the relative ionization is proportional to the molar number. The relative ionization for x-rays in many cases is much higher than that given by the molar number relation. This is very probably due to the ionization from secondary radiation. Table III, based on Kleeman's paper,

[3] Kossel, Ann. der Phys. **37,** 393 (1912)
[4] Lenard, Ann. der Phys. **56,** 255 (1895)
[5] Strutt, Phil. Trans. **195.** 507 (1901)
[6] Kleeman, Proc. Roy. Soc. **79,** 220 (1907)

gives the relative ionization $1/K$, with air taken as unity. The molar number N is given in the second column, while the last column gives the product KN. These results are plotted in Fig. 4. While there is a considerable departure from the linear relation for several of the values, it is evident that for the case of these ionizing agents the relative ionization is also approximately proportional to the number of electrons per molecule.

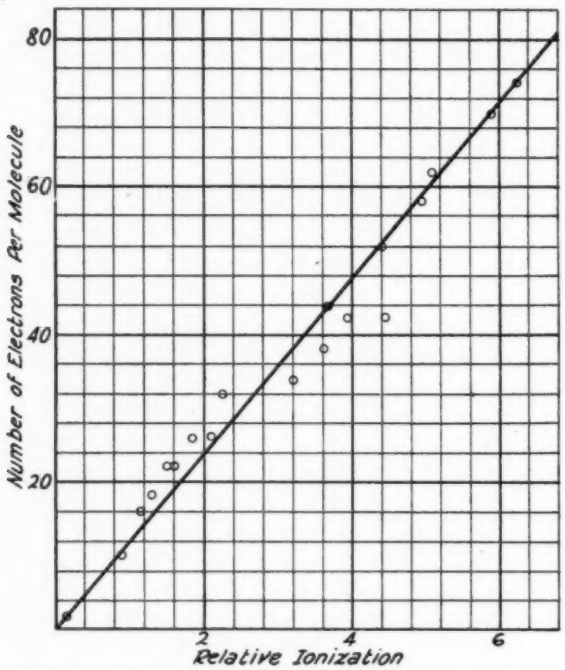

Fig. 4. Kleeman's results for the relative ionization by β-rays in various gases as a function of the number of electrons per molecule.

Vapor Pressure Measurements with the Ionization Gauge

Measurements of the vapor pressure of vacuum oils at different temperatures have been made by Mr. Huthsteiner, of this laboratory. Assuming a composition corresponding to the formula $C_{12}H_{26}$ ($N=98$) which seems reasonable from the observed boiling and freezing points of the oil, vapor pressures were calculated from ionization gauge readings. The values obtained ranged from .01 to 0.1 bar at 0°C and from 0.2 to 2.0 bars at 25°C.

Measurements of the vapor pressure of napthalene ($C_{10}H_8$), $N=68$, obtained by Mrs. McLane are given in Table IV and are in fair agreement with the published data of Barker[7] and Allen.[8]

[7] Barker, Zeit. Phys. Chem. **71**, 235 (1910)
[8] Allen, Journ. Chem. Soc. **77**, 412 (1900)

TABLE III

Relative ionization due to β-rays in various gases (after Kleeman).

Gas	*N*	*1/K*	*NK*
H_2	2	0.16	12.5
NH_3	10	0.89	11.2
Air	(14)	1.00	14.0
O_2	16	1.17	13.6
CO_2	22	1.60	13.8
C_2N_2	26	1.86	14.0
N_2O	30	1.55	19.3
SO_2	32	2.25	14.2
CS_2	38	3.62	10.5
Methyl Alcohol	18	1.69	10.6
Ethyl Aldehyde	32	2.12	15.0
Ethyl Chloride	34	3.24	10.0
Ethyl Ether	42	4.39	9.6
Pentane	42	4.55	9.2
Benzene	42	3.95	10.6
Methyl Bromide	44	3.73	11.2
Ethyl Bromide	52	4.41	11.8
Chloroform	58	4.94	11.8
Methyl Iodide	62	5.11	12.1
Ethyl Iodide	70	5.90	11.9
C Cl_4	74	6.28	11.8

TABLE IV

Vapor pressure of napthalene

Temperature	Vapor pressure	
	Ionization gauge	Barker and Allen
18°C	85 bars	106 bars
14	68	76
11	52	57
5	36.5	33
0	20	18.5
− 2.5	15.6	14
− 6	12.0	10
− 7	10.2	9.3
− 9.5	7.6	6.6
−10.5	7.3	6.0
−11	6.4	5.3

More recently, determinations of the vapor pressure of napthalene, at a temperature of about 30°C, have been made by Mrs. Mary Andrews. The method employed was similar to that used by Knudsen[9] for mercury. The results indicate that the above measurements, obtained by the ionization gauge, are a little high. This will be discussed more fully in a paper which Mrs. Andrews will publish in the near future.

[9] Knudsen, Ann. der Phys. **29**, 179 (1909)

We have measured the vapor pressure of water at temperatures ranging from $-50°C$ to $-78°C$. Scheele and Heuse[10] measured the vapor tension of water to a temperature as low as $-60°C$. If their values of $\log P$ are plotted against $1/T$, a straight line is obtained from which values of P may be extrapolated for lower values of T. The results obtained with the ionization gauge were found to agree with these values, if we assume $N=10$.

Similarly, our observations with mercuric iodide, HgI_2 agree with values obtained from published data by plotting $\log P$ against $1/T$ and extrapolating to the temperatures at which our measurements were obtained.

Efficiency of Ionization and Collision Frequency

According to the results of the measurements given above, the number of ions formed per unit volume, with a definite electron current, is proportional to the *total number* of electrons in the gas molecules per unit volume. Furthermore, for small electron currents, the number of ions at constant gas pressure, is proportional to the electron current. A simple interpretation of these observations would be that the collisions occur between electrons emitted from the cathode and electrons in the gas molecules. Assuming that every collision results in the formation of an ion, it is possible to calculate values of the mean free path of the electrons in different gases.

If L is the mean free path, then in traveling the distance d, the number of collisions is d/L. If i denotes the ionization current, and I the electron current,

$$d/L=i/I \quad \text{or} \quad L=dI/i.$$

In order to obtain measurements under conditions in which d would be definitely known, the outer grid of the gauge was made cathode, the cylinder anode, and the inner grid, the collecting electrode. For this arrangement $d=4$ mm. The value of the constant K for argon as given in the previous paper is $P/i=K=0.032$ when $I=20$ milliamperes. Hence $i/I=P/640$. That is, at 1 bar pressure, $d/L=i/I=1/640$. Hence $L=640\times d=256$ cm.

This, therefore, is the free path for argon at 1 bar pressure. On the other hand, the value of L at 25°C as calculated from considerations based on the kinetic theory of gases is $4\sqrt{2}\times 10.6=60$ cm (approx.) which is only about 24 per cent of the value derived from the measurement of the ionization current. This would lead to the conclusion that only

[10] Scheele and Heuse, Ann. der Phys. **29**, 723 (1909)

about 24 per cent of the collisions with molecules are effective in producing ionization.

The most interesting result of this investigation is the observation that under similar conditions of accelerating voltage, and electron current, and for the same arrangement of electrodes, the number of ions produced per unit electron current is (in most gases) approximately proportional to the total number of electrons per unit volume. We might conclude therefore that the probability of ionization on collision is proportional to the total number of electrons in the atom. The voltages used in the present investigation are obviously too low to enable the incident electrons to cause emission of electrons from the K or L ring of such an atom as that of mercury. This would lead to the view that the energy of collision is transmitted unaltered from the inner electron which has been stimulated to an external electron which is then ejected.

The experiments described in the present paper were performed about two years ago, but publication was delayed in the hope that further experiments could be carried out in order to interpret the significance of the observations described above. Such experiments are now under way, but it has been considered that there is sufficient interest in the results obtained so far to make them worth publishing even before the underlying explanation is fully understood.

RESEARCH LABORATORY OF THE
GENERAL ELECTRIC COMPANY,
SCHENECTADY, NEW YORK,
November 14, 1923.

ON THE COLOR OF THE SEA. II[1]

By Was. Shoulejkin

Abstract

Color of the sea.—*Spectrophotometric observations of the inner light diffused up from polar seas* were made, using a special instrument which enabled a direct comparison at various wave-lengths of the light diffused vertically up from the sea with the direct light from the sun and sky. The curves obtained agree well with the formula derived in the previous paper. *Measurements of the coefficient of diffusion made with the Secchi disk*, by means of the author's theory, agree with values of the coefficient a determined from laboratory data for the Indian ocean (by Ramanathan) and for the pure water of the Sargass Sea (compared with a for distilled water according to data given by Martin). Recent papers by Raman and by Ramanathan, who consider exclusively molecular scattering, are discussed. When the intensity of the diffused inner light is small, the color of the sea depends almost entirely upon light reflected from the sky.

Complementary relation of the color of deep-sea plants and corals to that of the light transmitted to them.—The coefficient of reflection of a leaf of *laminaria* from the bottom of Warneck Bay varies with wave-length very closely in proportion to the reciprocal of the intensity of the illumination at that depth computed from spectrophotometric data. In the case of *Mediterranean coral* from a depth of about 70 meters, good agreement was also found up to .59μ above which the illumination is extremely weak.

IN my preceding article published in this journal[2] it was shown that the bright color characteristic of every sea or lake can be quite easily explained by certain well known optical phenomena taking place in the sea-water and on its surface. Necessary correlations were also drawn which enabled an observer looking at the sea to calculate the spectrum of light, using coefficients easily determined from the experiment. Thus if both the dependence of the coefficient of absorption of rays in pure water $f(\lambda)$ upon the length of the wave corresponding to the given part of the spectrum (given in graphical form), and the Rayleigh's coefficient a of light scattering in sea-water for wave-length μ and for a depth z of 1 meter are known, then the spectrum can be calculated by means of a formula, reproduced here below, after having made some transformations

$$\frac{M_0}{S_0+H_0}=\frac{1}{\pi}\,\frac{\frac{1}{4}\,a/\lambda^4}{\frac{1}{4}a/\lambda^4+f(\lambda)}\,. \tag{4}$$

The fraction on the left side of this equation represents the ratio, which is sought, of the intensity of illumination of the sea from below

[1] Communicated to the Scientific Institution of Moscow, October 2, 1922

[2] Shoulejkin, Phys. Rev. **22**, 85 (1923)

by the inner diffused light (M_0) to that from above by the sun (S_0) and the sky (H_0).

Eq. (4) relates to the case of particles suspended in the sea-water which are so very small that they cause only a scattering of light according to the law of Lord Rayleigh. But if, together with such particles, there are bigger particles of the second kind in the water which cause a selective reflection and selective absorption of light, the calculations of the spectrum must be carried out by means of a more complicated formula

$$\frac{M_0}{S_0+H_0}=\frac{1}{\pi}\,\frac{(1-\beta)\frac{1}{4}a/\lambda^4+\beta\frac{1}{2}\varphi(\lambda)}{(1-\beta)\frac{1}{4}a/\lambda^4+f(\lambda)+\beta[1-\varphi(\lambda)]} \tag{5}$$

where φ (λ) represents the coefficient of reflection (given in a graphical form) for the substance forming the particles of second kind, and β a coefficient dependent upon their concentration.

In the preceding article I have already described the first experiments which served for the proof of the theory by tests in the laboratory. It was desirable to verify the theory on a larger scale, directly in the sea. For this purpose a special sea spectrophotometer was designed by the author and constructed in the workshop of the Physical Institution.

The Sea Spectrophotometer

The general appearance of the apparatus is shown by Fig. 1. The tripod S on which it is fastened is screwed to the deck in such a manner that the objective M of the apparatus is stretched out overboard and directed perpendicularly to the surface of the sea. The diffused inner light emitted from the latter, reaches the objective and after passing through a system of total reflection prisms and of lenses (a system resembling the periscope of a submarine), enters one of the slits k'' of the double collimator $k'k''$. Into the other slit of this collimator enters the light from the ground-glass which covers the camera H at the top and which is illuminated from above with the same light from the sun and sky as is the sea. Then the two rays to be compared pass from the collimator through the usual optical system of a spectrometer, being refracted by a Wollaston prism inclosed in a cylindrical camera P. An observer looking through the eyepiece O sees two spectra lying directly one above the other, the spectrum of the light falling on the sea from above (S_0+H_0) and that of light coming from the depth of the sea (M_0).* With the aid of a special slit inclosed in the ocular tube, a monochromatic strip can be selected from both spectra of wave-length easily determined with the aid of the vernier of an alidade sliding on

* The apparatus was shielded from reflected skylight by means of a screen.

the limb L and attached to the tube O which can rotate about a vertical axis, and thus monochromatic spectral rays be directed to the eye of an observer. Making the well known simple calculations for the different positions of the tube O corresponding to the different wave lengths λ, we shall find the experimental spectrum curve for the given sea.

Experiments at Sea

Preliminary measurements, with the aid of the apparatus just described were made by the author in the Black Sea near Sebastopol on board the cutter *Aj-Phoka*, in June 1922. The results of observations

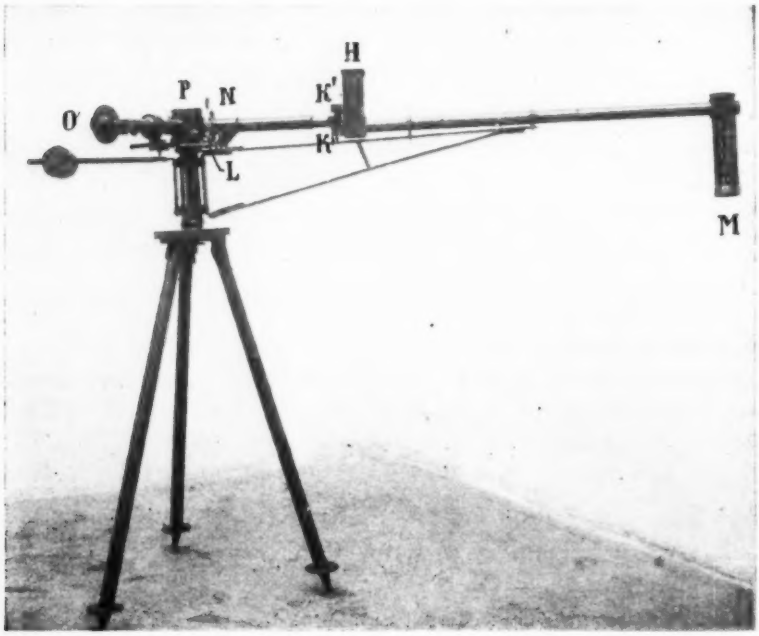

Fig. 1.

agreed sufficiently with the theory, but, unfortunately, the weather was extremely unfavorable, and owing to the violent rolling, the observations were but little trustworthy for plotting accurate curves.

Under far more favorable conditions I succeeded in making experiments on board the hydrographic ship *Pakhtusov* which left Archangel on August 22 1922 for the purpose of supplying the radio stations of Jugorsky-Shar on the north shores of the Island Vajgatsh and the peninsula Jamala on the cape Nare-Sale. Along with the spectrophotometric measurements there was made an approximate determination of the coefficient of scattering by means of a Secchi disk, on the basis of

considerations indicated in my first article. But the latter must be regarded in some measure as provisional, for in polar seas, together with the particles of first kind there must be supposed a considerable quantity of particles of the second kind which introduce errors in the results of observations. However, these errors should not be considerable for it is likely that there are plenty of particles of the second kind in certain Bavarian lakes explored by O. v. Aufsess, and yet the depth of disappearance of the Secchi disk in these lakes (given by that author) coincides sufficiently with the depth calculated according to our theory as was noted in my preceding article.

The data obtained on four stations of observation are collected in the following table as examples.

No.	Situation of Station	Time	Depth of disappearance of the Secchi disk	α
1	Extreme north part of White Sea, Lat. 66°34′N; Long. 41°24′ E	9 A.M.	8 meters	0.09
2	Jongorsky-Shear, Warneck Bay	3 P.M.	5	0.23
4	Kara Sea, near Isle of Voronov	10 A.M.	12.5	0.03
5	Kara Sea, Lat. 69°52′ N; Long. 62°45′ E	10 A.M.	11	0.05

The spectral curves obtained at these four stations* are shown in Fig. 2. Two dotted curves lying one above and another below the experimental ones, are constructed theoretically for two different assumed values of α and β. As may be seen, the group of experimental curves lie quite well within the limits of theory. As a matter of fact the absolute intensities of the inner diffused light are everywhere less than given (for instance curve 8, which was constructed in the first article for the White Sea, supposing that only particles of first kind uniformly distributed in the water are present), but such systematic divergence is fully explained by the mere fact of the presence of particles of the second kind which selectively absorb the light. There could even be found an assumed value of β for which the theoretical curve would go exactly through the experimental points, but there is no special interest in this, for we know that the distribution of particles of both kinds is *not uniform* in layers of seawater at different depths.

* It would have been very interesting to make measurements in the Barentz Sea northward of the Island Kolgujev, but unfortunately it was impossible owing to the very violent rolling.

Application of the Theory to Investigation of the Coloring of Deep-Sea Animals and Plants

Long ago it was noted that the greater the depth at which a given species is found the redder is its color, and the assumption was made that such a color is just complementary to the light which reaches this depth. It is obvious that having the optical constants characteristic of given waters, it is possible to calculate the spectrum of light falling on the given animal or plant after having passed through a layer of sea-water of more or less depth.

If the color of an animal or plant is complementary, then the coefficient of reflection for its surface must be inversely proportional to the intensity of each corresponding spectral ray which reaches the depth. This is in fact the case as is shown by the results of our experiments.

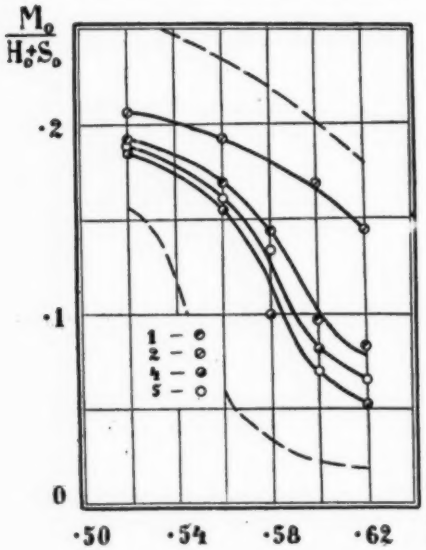

Fig. 2. Spectral curves for four stations.

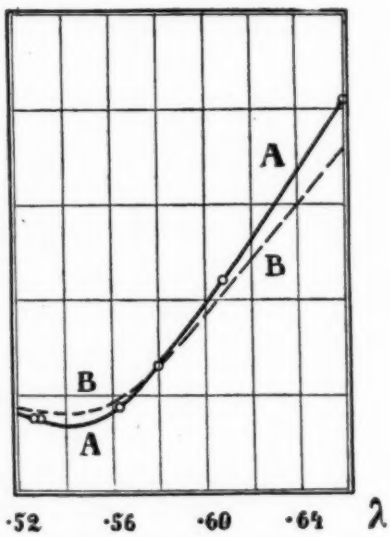

Fig. 3. Coefficient of reflection for Laminaria.

Let us for example take the curve AA, Fig. 3 which represents the coefficient of reflection found for a leaf of the plant *Laminaria*, taken from the bottom of the Warneck Bay. In the same figure a calculated curve BB shows by a dotted line the ordinates which are inversely proportional to the intensity of rays reaching the bottom of the bay. As can be seen, both curves lie very near one another, and therefore taking into consideration the above mentioned correction, we must conclude that this leaf of *Laminaria* is really colored in the complementary color.

Unfortunately there were no arrangements for dragging on board the *Pakhtusov*, and I could not get different animals and plants to examine their colors. Therefore I shall give some spectrophotometric data concerning coral of the Mediterranean, that was supplied to me. In Fig. 4 a continuous curve is shown representing its coefficient of reflection determined experimentally. In the same figure are seen two dotted curves, the ordinates of which are inversely proportional to the intensities of spectral rays reaching the depth, one corresponding to the depth 50 meters and the other to 100 meters. As can be seen, the experimental

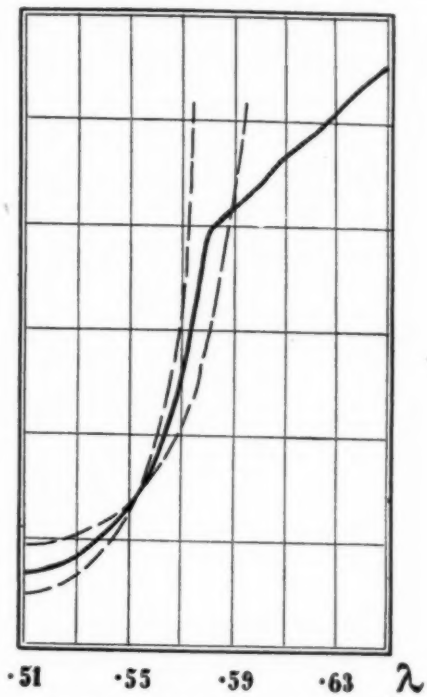

Fig. 4. Coefficient of reflection of Mediterranean coral.

curve to wave-length 59μ runs between these limiting curves, which confirms our hypothesis, for the given specimen, it appears, was found at a depth between 50 and 100 meters. It is particularly interesting to note that the coral follows the spectrum of light falling upon it to wave-length .59μ, but beyond this where the intensity of the falling light rapidly decreases towards the red end of spectrum and the ordinates of the dotted curves, being inversely proportional to the same, rapidly increase, we see that the curve of coefficient of reflection bends aside and no longer increases regularly.

Discussion of Papers by Raman and Ramanathan

After the first account of my investigations had been sent to the Physical Review, an article of Prof. Raman[3] of Calcutta upon "The Color of the Sea" was received, and I also became acquainted with the experimental investigations of Mr. Ramanathan[4] concerning the same problem. Raman and Ramanathan consider exclusively the molecular dispersion in the waters of the sea and they deduce a formula for the emitted diffused light, disregarding secondary diffusion, which leads to a distorted spectral curve.

In seas which I have studied, the molecular scattering is only a very small and negligible part of the whole scattering of light, which is chiefly caused by more active agents. Thus for the most transparent, the Black Sea, the coefficient of diffusion is $\alpha = 0.004$ ($\lambda = 1\mu$; $z = 1$ meter) whereas the molecular diffusion gives only $\alpha = 2.9\ (10)^{-4}$.

I am studying now by laboratory methods the different types of scattering in natural waters, a study whose results will be published later. Here I should like to mention only that I cannot agree with Ramanathan who thinks that particles of matter suspended in water do not influence noticeably the color of the sea, reflecting most of the energy of light downwards. It is easy to see that the unsymmetrical diffusion discovered by him does not alter the line of arguments leading to my fundamental equation (4). Actually, the coefficient α is determined experimentally, taking into account only the part of the light energy which is reflected backwards in relation to the falling rays, but this part influences the color of the sea. The coefficient α thus loses perhaps the exact meaning given to it by Rayleigh.

The correctness of this view is confirmed by Fig. 6 of my first article, obtained experimentally with particles very much coarser than those in the sea-water. My theory of the Secchi disk is also confirmed in the article of Ramanathan himself. Calculated from his data, the coefficient α comes out 0.002, which according to the curve of Fig. 5 of the first article gives for the depth of disappearance of the Secchi disk $z = 50$ meters, and at this depth, according to J. Shokalsky, the disk really disappears in the waters of the Indian ocean. The greatest depth of the disappearance of the disk was observed in the Sargass Sea, where it reached $z = 66$ meters, corresponding according to my theory to $\alpha = 1.3\ (10)^{-3}$. A figure of the same order was obtained by me from the data of Martin[5] for distilled water.

[3] Raman, Proc. Roy. Soc. London **A101** (1922)
[4] Ramanathan, Phil. Mag. (1923)
[5] W. H. Martin, Journ. Chem. Soc. 1922

Therefore both for the most turbid Bavarian lakes investigated by O. v. Aufsess and for the most transparent point of the ocean my theory gives correct results, although the coefficient α varies from $1.46(10)^{-1}$ to $1.3(10)^{-3}$.

Returning to the case of molecular scattering I should point out that where it happens in its purest form (in the most transparent parts of the ocean), the energy of light emitted from the sea is very small in comparison with the energy of light *reflected by the surface of the sea* (as by the surface of a black mirror), and the color of the sea will depend here chiefly upon the color of the sky (see section 5 of the first article.)

In conclusion I wish to give my thanks to the Commitee of the Floating Marine Scientific Institute which gave me the opportunity to do experimental work in the polar Seas, and to all establishments and persons who helped me in my work either on the polar seas or in the Black Sea.

PHYSICAL DEPARTMENT
OF THE SCIENTIFIC INSTITUTION,
MOSCOW,
October 27, 1923.

NOTE ON THE ALTERNATING CURRENT RESISTANCE OF SINGLE LAYER COILS

By S. Butterworth

Abstract

In a previous paper[1] a formula was derived which involved a function u_n whose values were given only for coils with a length b not greater than the diameter $2a$. Values are now given *for longer coils* with values of $b/2a$ from 1 to ∞. The original formula is also modified to include *closely wound coils* by the introduction of new coefficients whose values are given for various ratios of the wire diameter d to the wire spacing D. Comparison of computed values with measurements made by Hickman[2] for coils with $b/2a$ between 3 and 12, shows for the original formula a maximum discrepancy of +30 per cent (instead of 300 per cent as given by Hickman) and for the modified formula an average difference of only +7 per cent (calc. −obs.).

IN a paper published recently by the Bureau of Standards[2] C. N. Hickman has made a comparison between the measured and computed values of the alternating current resistance of single layer coils and for this purpose makes use of a formula published by the present writer.[1] From Hickman's Table IV it appears as if the writer's formula was in error by as much as 300 per cent in certain cases. In the present note it will be shown that this difference is due mainly to a misinterpretation of the scope of the formula, and that when the formula is legitimately applied the difference is of the order 30 per cent in the worst case, and this is the true magnitude of the error involved due to the assumption of "uniform field" made in establishing the formula.

Hickman's observations relate to coils for which the length is at least three times the diameter, whereas the numerical values given by the writer for use in his formula were clearly only intended to apply to short coils, that is for coils for which the length is less than the diameter. The formula may however be adapted to long coils by computing further values of the factor u_n which is a function of the shape of the coil.

The formula in question is

$$R' = R\{1 + F(z) + u_n G(z) d^2/D^2\} \tag{1}$$

$$z^2 = 2\pi^2 f d^2/\rho \tag{2}$$

in which R' is the alternating current resistance of the coil, R the direct current resistance, f the frequency of the alternating current, d the diame-

[1] S. Butterworth, Phil. Trans. London A **222**. 57, 1921

[2] C. N. Hickman, Bur. Stand. Sci. Paper No. 472

ter, ρ the resistivity of the wire of the coil, and D the spacing between turns, all being in c.g.s. units. $F(z)$ and $G(z)$ are functions of z tabulated in the appendix, and u_n is a factor depending on the ratio of the coil length b to the radius a. This is also tabulated in the appendix. In the writer's previous paper the values of u_n were given only up to $b/2a=1$, and throughout the range $b/2a=0$ to $b/2a=1$ the approximate formula

$$u_n=3.29+b/a \tag{3}$$

was recommended. This formula is the one apparently used by Hickman, although its use is not valid with coils for which $b/2a$ exceeds 3.

The values of u_n now given for the longer coils have been calculated by the same methods as those used for the shorter coils[3] making use of the known elliptic-integral formulas for the transverse and tangential components of the field on the surface of a solenoid.

In the derivation of formula (1) it was assumed that the field acting on an individual wire of the coil could be regarded as uniform and equal to that produced by the whole coil at the centre of the wire under consideration, so that its use is limited to coils for which the spacing is not too close. It was deduced however from general reasoning[4] that the error due to the assumption of "uniform field" can be neglected even for closely wound coils when the frequency of the current is low, the criterion for low frequency being that z is less than unity.

A more detailed investigation of the effect of field curvature has now been made by the writer with the result that the "uniform field" formula (1) must be replaced by the formula[5]

$$R'/R=\alpha\{1+F(z)\}+(\beta u_{1n}+\gamma u_{2n})G(z)d^2D^2. \tag{4}$$

Where u_{1n} is that portion of u_n arising from the field normal to the axis of the coil, u_{2n} is the portion due to the field tangential to the axis and α,β,γ are functions of z and d/D approximating to unity when d/D is small.

Values of α,β,γ are given in Table IV. The writer hopes shortly to be able to publish the mathematical treatment leading to these values.

The following table corresponding to Table IV of Hickman shows how the "uniform field" formula (1) and the extended formula (2) compare with Hickman's observations.

It is seen that the "uniform field" formula (1) gives results always higher than those observed, the difference increasing with frequency to

[3] Butterworth, l.c.,[1] section 15

[4] Butterworth, l.c.,[1] section 5

[5] The computed values of the formula functions refer to the case where the number of turns is very large. The formula will give wrong results for coils of a few turns.

TABLE I

Values of R'/R for single layer solenoidal coils

Length $b=96$ cm; wire diameter $d=0.518$ cm; spacing $D=0.6$ cm.

Coil diameter	Frequency per sec.	Computed Eq. (1)	Computed Eq. (4)	Observed Hickman
8.24 cm	1000	1.81	1.72	1.69
	2000	3.11	2.65	2.50
	3000	4.10	3.19	3.04
15.8	1000	1.76	1.68	1.59
	2000	2.96	2.58	2.33
	3000	3.88	3.13	2.88
22.6	1000	1.70	1.64	1.55
	2000	2.86	2.54	2.28
	3000	3.74	3.12	2.84
30.4	1000	1.63	1.59	1.54
	2000	2.74	2.51	2.40
	3000	3.58	3.16	2.75

about 30 per cent at 3000 per second. The corrected formula (4) gives results which on the average are 7 per cent higher than those observed. There is no tendency however for the difference to increase with frequency so that the difference may be experimental rather than real.

The formula recommended in this paper differs from that deduced by Hickman in that the resistance calculated is that of the whole coil, and not that of the central wire. For long coils the central wire resistance may approximate the average resistance of the coil, but for short coils,

TABLE II

Values of $F(z)$ and $G(z)$

z:	0–0.5	0.5	1.0	1.5	2.0	2.5
$F(z)$:	$z^4/192$	0.000326	0.00519	0.0258	0.0782	0.1756
$G(z)$:	$z^4/64$	0.000975	0.01519	0.0691	0.1724	0.295
z:	3.0	3.5	4.0	4.5	5.0	>5
$F(z)$:	0.318	0.492	0.678	0.862	1.042	$(\sqrt{2z-3})/4$
$G(z)$:	0.405	0.499	0.584	0.669	0.755	$(\sqrt{2z-1})/8$

TABLE III

Values of u_{1n} u_{2n} u_n for solenoidal coils

a = radius of coil; b = length of coil.

$b/2a$:	0	0.2	0.4	0.6	0.8	1.0
u_{1n}:	3.29	3.13	2.83	2.51	2.22	1.94
u_{2n}:	0	0.50	1.23	1.99	2.71	3.35
u_n :	3.29	3.63	4.06	4.50	4.93	5.29
$b/2a$:	2	4	6	8	10	∞
u_{1n}:	1.11	0.51	0.31	0.21	0.17	0
u_{2n}:	5.47	7.23	8.07	8.52	8.73	9.87
u_n :	6.58	7.74	8.38	8.73	8.90	9.87

the losses in the end turns are of the first importance. Furthermore Hickman's replacement of a solenoid by two straight parallel systems leads to an uncertainty in some of his numerical constants so that real differences between theory and observation may be masked by this uncertainty.

TABLE IV

Values of α, β, γ

$\frac{d}{D}$	$z=1$			$z=2$			$z=3$		
	α	β	γ	α	β	γ	α	β	γ
1.0	1.01	1.02	0.96	1.09	1.34	0.67	1.31	2.29	0.49
0.9	1.00	1.02	0.97	1.06	1.29	0.72	1.20	1.99	0.55
0.8		1.02	0.98	1.04	1.23	0.78	1.13	1.73	0.62
0.7		1.02	0.98	1.02	1.18	0.83	1.08	1.52	0.68
0.6		1.01	0.99	1.00	1.13	0.87	1.04	1.36	0.75
0.5		1.01	0.99		1.09	0.91	1.02	1.24	0.82
0.4		1.01	0.99		1.06	0.94	1.01	1.14	0.88
0.3		1.00	1.00		1.04	0.97	1.00	1.06	0.93
0.2					1.01	0.99		1.03	0.97
0.1					1.00	1.00		1.01	0.99

$\frac{d}{D}$	$z=4$			$z=5$			$z=\infty$		
	α	β	γ	α	β	γ	α	β	γ
1.0	1.43	3.61	0.43	1.50	4.91	0.41	1.71	inf.	0.35
0.9	1.30	2.75	0.49	1.37	3.39	0.46	1.55	12.45	0.39
0.8	1.21	2.12	0.55	1.25	2.48	0.53	1.41	4.83	0.44
0.7	1.12	1.71	0.62	1.15	1.94	0.60	1.27	2.87	0.52
0.6	1.07	1.51	0.70	1.09	1.60	0.68	1.16	2.03	0.60
0.5	1.03	1.32	0.78	1.04	1.37	0.76	1.08	1.59	0.69
0.4	1.02	1.19	0.85	1.02	1.22	0.84	1.03	1.33	0.78
0.3	1.00	1.10	0.91	1.00	1.11	0.90	1.01	1.17	0.87
0.2		1.04	0.96		1.05	0.96	1.00	1.07	0.94
0.1		1.01	0.99		1.01	0.99		1.02	0.98

DEPARTMENT OF SCIENTIFIC RESEARCH AND EXPERIMENT,
ADMIRALTY, S. W. 1, LONDON, ENGLAND.
November 19, 1923.

DURATION OF IMPACT OF A PAIR OF BARS OF STEEL AND OF COPPER

By E. W. Tschudi

Abstract

The two bars to be tested were hung by bifilar suspensions and the duration of impact (less than .0007 sec.) was measured for various impact velocities from records of the current through the surface of contact, made with a *special heavy tungsten wire oscillograph* with an undamped frequency of 16,000 per sec. The electrical resistance of the contact was shown to be independent of the velocity. The results for *steel bars* are from 10 to 20 per cent higher than those obtained previously with a condenser method of time measurement. The duration was the same for a bar 9 cm long as for one of the same mass 62 cm long. This seems to contradict the compressional wave theory. For two *copper bars* the duration came out 1.4 times that for steel bars of the same dimensions and velocity of impact, the ratio being the same as that of the velocities of sound in the two metals.

I. Introduction

IN a previous paper[1] experimental results of the duration of impact of bars were given which showed that the compressional wave theory was inadequate to explain the reactions within bars during an end on collision. The measure of these short time-intervals was established by a determination of the charges accumulated on a condenser connected in series with the two suspended bars, with a battery and with suitable resistance. The charging equation for a condenser,

$$t = RC \log [1/(1-q/cV)] \qquad (1)$$

was employed. Calculations were made with the tacit assumption that the resistance R remained constant during the collision and that it had the same value as when the two bars were fixedly held in contact. Records made with an oscillograph show that the first part of this assumption at least is valid.

II. Oscillograph Measurements[2]

An oscillograph element of heavy tungsten wire, with an undamped frequency of 16000 cycles per second, was joined in series with a source of potential of 24 volts and with two machinery steel bars of length 61.8 cm and diameter 2.54 cm, whose ends were machined plane. The bars were each hung from knife edge supports by two bifilar suspensions

[1] E. W. Tschudi, Phys. Rev. **18**, 423 (1921)

[2] This work was performed in the laboratory of Dr. E. A. Eckhardt, Bureau of Standards, Washington, D. C.

made of fine copper wire. When at rest, both bars were coaxially orientated so that their plane ends touched.

An element of high frequency was essential because the duration of the whole phenomenon to be recorded was less than .001 second and the current variations within this period were exceedingly rapid. The resistance of the entire non-inductive circuit was less than two ohms; the current time lag was consequently negligible in comparison with the duration of impact. The unusually high frequency was obtained by the use of a specially constructed element with a fret distance of 0.8 cm and by applying a tension to the heavy tungsten wire relatively far in excess of the customary amount.

Due to summer temperatures the usual damping fluid, made of castor oil and turpentine—and even pure castor oil, failed to damp the element critically. Numerous solutions, such as of glucose, starch, ethyl malate and others, were tried, but all of these failed in their purpose, because

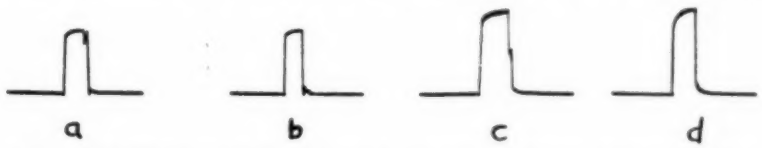

Fig. 1. Oscillograms showing contact resistance between steel and copper bars during impact.

they were insufficiently transparent, or because they dissolved the mirror cement, or changed their consistency with age, or because their damping showed peculiarities which indicated that the damping force could not be considered proportional to the velocity. Finally blown peanut oil was found to satisfy all of the requirements.

A rotating drum camera[3] with a circumference of 1.52 meters and with a peripheral speed of about 1000 cm per second was employed to record the deflections of the element. In addition to the rotary motion, the drum was given a translatory motion along its axis during the time of exposure of the film. A tuning fork of frequency 500 served to produce a suitable time scale on the moving film.

Copies of some of the oscillograms obtained are shown in Fig. 1 where it is seen that the resistance at the point of contact of the two bars during impact is practically constant, since the transverse portions of each of the records approach parallelism. The record of the impact of the two machinery steel bars colliding with a relative initial velocity of 12.5 cm per second is given by *a*; *b* is the record when the relative initial velocity is 47.7 cm per second; *c* and *d* are records for the case of copper bars of

[3] E. A. Eckhardt, Jour. Franklin Inst., July, 1922

length 61.0 cm and diameter 2.54 cm, colliding with relative initial velocities of 6.4 cm and 56.2 cm per second respectively. The curvatures on the records at the termination of each current change, are attributed to a slight overdamping of the element. The slope of the transverse portions of the records was caused, no doubt, by the inertia lag of the element. Any deviation from parallelism of the two faces in contact during a collision was registered as a zig-zag effect.

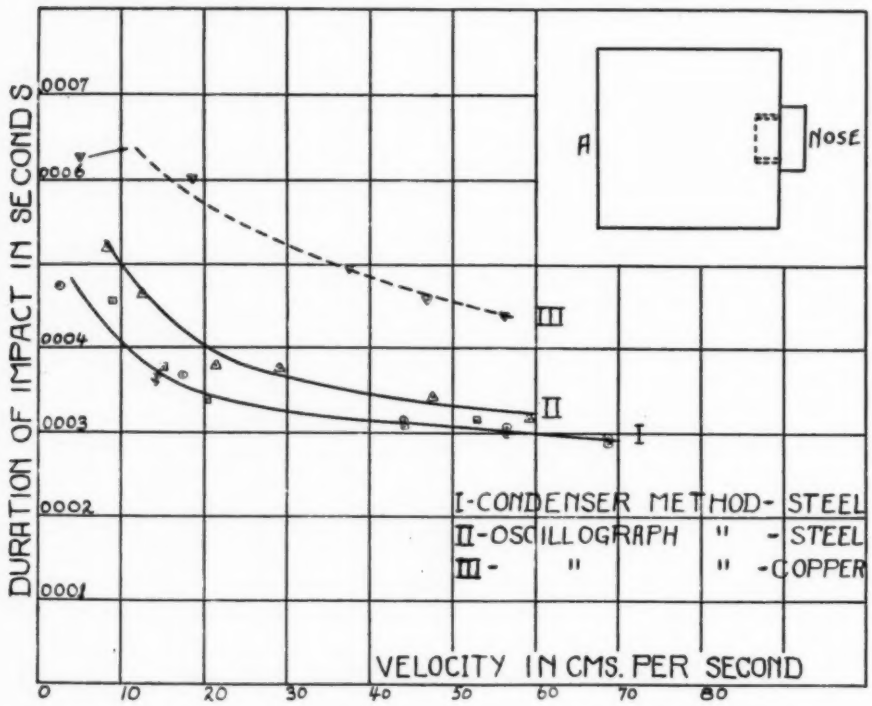

Fig. 2. Dependence of duration of impact of bars upon relative velocity at impact.

III. Comparison of Results Obtained By Condenser and Oscillograph Methods[4]

The dependence of the duration of impact upon the relative initial velocity between the two steel bars in impact, as determined by two distinct methods, is given in Fig. 2, Curves I and II. Curve I was obtained by the condenser method and Eq. (1); Curve II represents results obtained with the oscillograph. The broken Curve III shows oscillograph results for the above-mentioned copper bars. In order to determine the duration of impact from the oscillograms, the width of each peak was

[4] Experiments with condenser method were performed in the Physical Laboratory of Johns Hopkins University.

measured close to its base and close to its summit. The average of these two measurements was then compared with the time scale on the film.

The discrepancy between Curves I and II is somewhat difficult to explain. Three different galvanometers were used in connection with the condenser method. All results given by them lie close to Curve I. The discrepancy would be accounted for if the contact resistance when the bars are held in contact is smaller than the resistance when the bars collide.[5]

Comparison of Curve I with the curve for the same steel bars given in an earlier paper,[6] will disclose the fact that values of the duration of impact given by the latter are greater than those given by Curve I. In the earlier experiments a slide wire rheostat of appreciable inductance was used in the charging circuit, so that conditions existed which did not warrant the use of Eq.(1). Hence the quantitative results given in the earlier paper are erroneous though qualitatively they agree with the present results.

A cylindrical steel body, a sketch of which is given in Fig. 2, was substituted for one of the steel bars. Its mass was very nearly the same as that of the replaced bar but its entire length was only 9.1 cm. The diameter of the cylindrical nose equalled the diameter of the remaining bar. Results, by the condenser method, for this arrangment are indicated in Fig. 2 by points surrounded by small squares. In observing Curve I and the proximity of the last mentioned points to it, one can no longer admit any basis for the compressional wave theory. Results were not different when the bar was allowed to strike against the face *A* from those when it struck the nose.*

The writer is greatly indebted to Dr. E. A. Eckhardt for his interest in this problem, which led to the investigation of contact resistance, and for the use of the extensive facilities and equipment which his laboratory offered. He also wishes to express his thanks for the helpful suggestions given by Professor J. S. Ames in the preparation of this manuscript.

JOHNS HOPKINS UNIVERSITY,
January 21, 1924

[5] Bureau of Standards calibration at 1000 cycles of the Leeds and Northrup microfarad condenser shows that its capacity is .98899 microfarads. This discrepancy could not possibly explain the differences between curves I and II.

[6] Tschudi, loc. cit.,[1] p. 426, Fig. 3

* Curves II and III were obtained by the same method for bars of practically the same size but of steel and copper respectively. The ratio of the ordinates is practically constant and equal to 1.4. This value is also that given in the Smithsonian Tables for the ratio of the velocities of sound in the two metals.—Ed.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE WASHINGTON MEETING, APRIL 25 AND 26, 1924

The 127th meeting of the American Physical Society was held at the Bureau of Standards, Washington, D. C., on April 25 and 26, 1924. The President of the Society, Professor Charles E. Mendenhall, presided. Morning and afternoon sessions were held with an attendance of about three hundred.

On Friday evening the Society held an informal dinner commemorating the 25th anniversary of its founding. The speakers were M. I. Pupin, Henry Crew and R. A. Millikan. The dinner was attended by 186 members and guests.

The regular meeting of the Council was held on Friday, April 25, 1924. The following were elected to Membership: Samuel K. Allison, Colin Barnes, Charles H. Burr, W. P. Dobson, G. H. Glidden, Frederick R. Gorton, Ralph de L. Kronig, John T. Lay, Donald G. MacGregor, A. Appleton Packard, Mark L. Raymond, Charles H. Thomas, Arthur P. R. Wadlund, Arthur H. Warner, Richard H. Wilson, J. G. Winans.

The regular scientific session consisted of 90 papers, abstracts of which are given on the following pages. Abstracts 8, 19, 23, 27, 30, 46, 54, 55, 60, 63, 83, 86 and 89 were received too late to be put in the program, and these and 12 other papers were read by title. An **Authors Index** will be found at the end.

HAROLD W. WEBB, *Secretary.*

ABSTRACTS OF PAPERS

1. The width of the K absorption discontinuity in silver. F. K. RICHTMYER and R. C. SPENCER, Cornell University.—Several observers have found that the discontinuity in the x-ray spectral energy distribution curve, due to the introduction of an absorber into the beam, shows a "structure." Using the method of analysis discussed at the New York meeting (Feb. 1924) in connection with the width of spectral lines, it can be shown that, if we have a perfect crystal, a target with a uniform energy distribution, and a slit system of angular width α, then, if the absorber has a *perfectly* sharp discontinuity, showing no structure, (1) the width of the *observed* discontinuity should be equal to α, and (2) the shape of the energy curve through the discontinuity should be made up of two parabolas. Conclusion (1) has been verified

experimentally, from which it follows that, within the limits of error of measurement, the absorption discontinuity is perfectly sharp and shows no structure. Conclusion (2) has been verified so far as data permit. This work has been carried on by aid of a grant from the Heckscher Research Council of Cornell University.

2. The reflection of characteristic bromine x-radiation by a crystal of potassium bromide. S. K. ALLISON and WILLIAM DUANE, Harvard University.—The spectrum of x-rays from a molybdenum target tube operated at 63,000 volts and 2 m.a. has been obtained by reflection from the (100) planes of a small KBr crystal. In addition to the characteristic Mo K-series peaks which occur in the first 4 orders, peaks appear at angles calculated for the Br K-spectrum in the first 3 orders. Mo $K\gamma$ and $K\beta$ are separated in the second and higher orders, Mo $K\alpha_1$ and $K\alpha_2$ in the 3rd and 4th orders. In the third order Br $K\gamma$ and $K\beta$ are separated, but the Br $K\alpha$-doublet is not resolved. The resolving power for the Br lines is less than for those of Mo, but increases more rapidly for Br than for Mo as the order increases. The sharpness and definiteness of the Br reflections decrease markedly with increase in the width of the *ionization chamber* slit, while the widths of the Mo peaks are much less affected. This, at least partially, explains the negative results recorded by Mie and Walter, who have recently attempted to obtain photographic evidence of this phenomenon. The intensities of the Br lines apparently decrease much less rapidly with increasing order than those of the Mo lines.

3. Evidence as to the mechanism of characteristic radiation. GEORGE L. CLARK and WILLIAM DUANE, Harvard University.—New experiments on the reflection of x-rays characteristic of iodine by crystals of KI (a fact discovered by the authors two years ago) furnish evidence as to the optimum conditions for its detection and its fundamental mechanism. (1) The iodine spectrum through 5 orders from the (100) planes of KI, originally obtained with the ionization spectrometer, was completely verified. (2) The primary beam from a tungsten target at 68,000 volts passed through 1 mm of copper before striking the KI crystal. Experiments under these conditions with a calcite crystal show that the spectrum at 0.3737 A (the critical absorption wave-length of iodine) has negligible intensity, agreeing with the calculation from the absorption coefficient that 1 mm of copper reduces the intensity of a ray with a wave-length between the iodine $K\beta$ and $K\alpha$ lines to 1/10,000 of its value without the screen. In the resulting KI spectrum the strong absorption due to iodine no longer appears, but the iodine emission lines are definitely present, showing that the phenomenon is probably not due to resonance or selective reflection. (3) Experiments to define the conditions necessary for obtaining photographic evidence of the characteristic iodine reflection, notably a narrow slit in front of the plate, are described.

4. The ionization produced by x-rays in small ionization chambers. HUGO FRICKE and OTTO GLASSER, Cleveland Clinic Foundation.—The ionization produced by x-rays in a small ionization chamber is due to the secondary fast electrons partly from the walls and partly from the air of the chamber. The contribution of the walls is a function of the ratio of the mass absorption of the x-rays to the mass absorption of the secondary fast electrons in the material of the walls. Measurements have been made on chambers with a volume of 1 cc made of different pure elements (lighter than copper) and their salts, using x-rays of varying quality. From the obtained data the relative coefficients of true mass absorption of x-rays can be calculated. It is found that the true mass absorption is of two types, one proportional to the third power of the atomic number and one independent of the atomic number, the dominance of the latter type increasing in inverse relation to the wave-length. The results agree with Compton's recent theory of absorption and scattering of x-rays. A chamber made of ammonium nitrate +1 per cent potassium chloride gives the ionization current of a chamber having

walls of atmospheric air, and may be used as a standard ionization chamber in investigations of the biological action of x-rays.

5. A new form of current-measuring instrument of extreme sensitivity. ROY KEGERREIS, Mayo Clinic, Rochester, Minn.—The charged particles of an ionized gas are attracted to or repelled from the plates of an ionization chamber. Air currents are set up within the ionization chamber when this action takes place as was shown by Zeleny in 1898. This circulation phenomenon, which is commonly called "electric wind," is employed, in the present instance, to move the vane of a suspension system. The plates of the ionization chamber are perforated with numerous holes. Suitable passages are provided in order to cause the air currents from the ends of the ionization chamber to impinge upon a vane and thus twist the suspended system. Alpha rays from polonium are used to produce the ionization. It is essential that the conditions of ionization be such as to insure operation on the straight part of the saturation curve. The instrument has a sensitivity much higher than that obtainable with any type of galvanometer and is about equal to that which can be realized with a quadrant electrometer when shunted by a high resistance. It can of course also be used as a voltmeter. The same principles of construction may be adapted for extremely high voltage measurements by making use of similar attendant circulation phenomena in insulating fluids. It is necessary that the various parts be highly insulated from each other and so the preliminary working model was made from carvings in solid paraffin.

6. The scattering of x-rays. I. MAIZLISH, University of Minnesota.—In this paper the theories of Thomson, Debye and Schott are briefly summarized. The large-electron theory of A. H. Compton is criticized, and it is shown, among other things, that it leads to a value of m which is only 1/1000 of that obtained from the values of e and (e/m). An attempt is made to bring into harmony the known facts of x-ray scattering on the basis of classical electrodynamics. It is shown that if we assume the electron to be made up of a large number of parts and introduce into our equations of motion of these parts a term which is akin to friction in ordinary dynamics, we will be able to explain the observed diminution in the scattering coefficient when short wave-lengths are used. For long wave-lengths this will give the same scattering as Thomson's theory. But the observed asymmetry cannot be explained on this basis. It was next thought desirable to combine Debye's theory with our modified electron and to discuss the results. It appears impossible to adhere to classical electrodynamics and explain all known facts of the scattering of x-rays. (See J. Franklin Inst. May, 1924.)

7. The scattering of polarized x-rays by paraffin. G. E. M. JAUNCEY and H. E. STAUSS, Washington University.—G. E. M. Jauncey has shown (Phys. Rev., **23**, 313, 1924) on the basis of a corpuscular theory that the angle of scattering for complete polarization should be given by $\cos \phi_p = \alpha/(1+\alpha)$ where $\alpha = h/mc\lambda$. This theoretical prediction has been tested experimentally. X-rays were scattered from a paraffin block at about 88° and these polarized x-rays were scattered from a second paraffin block. The scattering from the second block was measured at different angles in a plane containing the electric vector. With x-rays of effective wave-length 0.25 A (measured by absorption in Al) a minimum was found at about 87° 30′, the theory predicting 84° 47′. The minimum reading, however, was not zero, this being due to multiple scattering, angular width of the primary rays, etc. These extraneous effects make the result somewhat uncertain. The experiment was repeated with x-rays of effective wave-length 0.54 A, the minimum then coming at about 90°, the theoretical value being 87° 30′. There seems therefore to be an experimental shift of the polarizing angle to the small angle side of 90° which increases as the wave-length decreases. The shift is less than the theory demands but is of the same order of magnitude.

8. The wave-length of molybdenum Kα rays scattered by light elements.—ARTHUR H. COMPTON and Y. H. WOO, University of Chicago.—The x-rays from a water-cooled molybdenum tube were scattered by a radiator placed about 3 cm from the focal spot. In one set of experiments, the following series of substances were used successively as radiators: metallic lithium, amorphous boron, graphite and water. These radiators were prepared in the form of cylinders of 8 mm diameter, the amorphous boron and the water being held by an oiled paper wall about .05 mm thick. The radiators were clamped successively in the same position, and scattered the rays at $128 \pm 2°$. The spectra observed showed in each case a faint line identical ($\pm .001$A) in wave-length with the primary Kα line, and a stronger line of wave-length greater by the amount $.039 \pm .001$A, as demanded by the quantum theory of scattering. Thus the quantum formula holds for the elements Li, B, C and O, contrary to the conclusion of Clark, Duane and Stifler. Experiments using successively sugar crystals and wood, which have about the same chemical composition, gave spectra in which the relative intensities of the modified and the unmodified lines were nearly identical, showing that their relative intensity does not depend upon whether the radiating substance is crystalline or amorphous.

9. A general quantum theory of the wave-length of scattered x-rays. ARTHUR H. COMPTON, University of Chicago.—The quantum theory of the change of wave-length of x-rays when scattered is extended to the case of scattering by bound electrons, by taking account of the energy spent in removing the electron from the atom in addition to that spent in setting the electron in motion. If the scattering electron and the residual atom can acquire any velocities consistent with the conservation of energy and momentum, the change of wave-length lies between $\lambda^2/(\lambda_s - \lambda)$ and ∞, where λ is the incident wave-length and λ_s is the critical ionization wave-length for the scattering electron in its original orbit. This result is identical with that of Clark and Duane's theory of tertiary radiation, and accounts adequately for all the observed modified lines. A restricted form of the theory is based on the assumption that the final momentum possessed by the residual atom is that acquired during the absorption from the incident beam of the energy hc/λ_s required to remove the electron from the atom. The resulting change in wave-length is $\lambda^2/(\lambda_s - \lambda) + \gamma$ vers ϕ, where ϕ is the angle between the primary and the scattered ray, and $\gamma = h/mc = .0242$ A. This formula describes accurately the spectra observed for rays scattered by the lighter elements.

10. The reality of the Compton effect. J. A. BECKER, E. C. WATSON, W. R. SMYTHE, R. B. BRODE and L. M. MOTT-SMITH, California Institute of Technology.—X-rays coming from a water-cooled molybdenum tube fall upon a plane sheet of aluminum placed about 6 cm from the target. The scattered radiation is analyzed by means of a calcite crystal in a Seemann spectrograph about 1 cm from the scatterer. The photographic plate is 42 cm from the crystal. The tube is operated at about 35,000 volts r.m.s. and 25 m.a. The angle between the incident and scattered rays is about 100°. A comparison spectrum of the molybdenum rays analyzed directly is also taken on the same film as the scattered radiation. The comparison spectrum shows the α_1, α_2, β and γ lines of Mo. A 60 hour exposure for the scattered radiation shows: (a) sharp α_1 α_2 lines clearly resolved and shifted by .027 A—this shift agrees very well with the Compton theory for 100°; (b) very faint unshifted α_1 α_2 line; (c) faint but unmistakable β line shifted .027 A. The resolved shifted α doublet cannot possibly be accounted for as tertiary radiation. This is then unambiguous evidence for the reality of the Compton effect.

11. Crystal structures and densities of oxides of the 4th group. WHEELER P DAVEY, Research Laboratory, General Electric Co.—(1) TiO_2 shows a base-centered tetragonal structure of Ti; $a = 4.582$ A; $a/c = .650$ (compare with Groth .6439). The

positions of the oxygens are indeterminate. Density of TiO_2 = 4.226 (compare with Groth 4.283).—(2) SnO_2 has a structure like TiO_2; a = 4.718 A; a/c = .670 (Groth .6726); density 7.036 (Groth 6.992 – 7.044).—(3) CeO_2 has a face-centered cubic lattice of Ce; a = 5.405 A; density 7.195 (Groth 6.93 – 7.99). The oxygens probably have the same spacing in CeO_2 that the fluorines have in CaF_2.—(4) PbO_2 gives a diffraction pattern which may be interpreted equally well as a TiO_2 structure, or as a body-centered tetragonal structure of Ti with undeterminate O. In either case a = 4.949 A and a/c = .685 (compare with Groth .676); the density is 9.498 (Groth 8.56).—(5) ThO_2 has the same structure as CeO_2; a = 5.585 A; density = 9.998 (Van Nostrand 9.876).—A diffraction pattern was obtained from ZrO_2 but so far no solution has been found. GeO_2 has not been tried. The only other member of this group which is crystalline at room temperatures is SiO_2. Infusorial earth heated to cone 11½ is a hexagonal close packed lattice (a = 6.80 A; a/c = 1.65) with apparently 6 SiO_2 per unit crystal, giving a density of 2.552. The exterior form given in Groth for tridymite can be derived from this lattice. The results of McKeehan for quartz are confirmed.

12. The orientations of electrodeposited crystals in iron, nickel, copper and zinc, as determined by x-rays. RICHARD M. BOZORTH, Research Laboratories of the American Telephone and Telegraph Co. and Western Electric Co., Inc., New York (Introduced by H. D. Arnold).—It is found that, whereas the crystals in electrodeposited copper and zinc are oriented at random, the crystals in iron and nickel deposits show preferred orientations. In nickel deposits the (100) planes tend to be parallel to the polished brass surface on which the deposits are made. In iron the (111) planes tend to have the same aspect. The method of investigation is to allow a beam of approximately monochromatic x-rays, having a circular cross-section, to fall obliquely on a foil stripped from the deposit, producing a characteristic pattern on a photographic plate placed normal to the incident beam a few centimeters behind the foil. A chaotic arrangement of crystals gives complete circles, as in the ordinary powder method, the intensity being constant along any one circle except as modified by absorption in the film. A preferential orientation is indicated by intensification at definite positions on the circles, different for each. The interpretation of the patterns is made in accordance with the geometrical analysis of Polanyi.

13. Apparatus for determining the orientation of single crystals. WHEELER P. DAVEY, Research Laboratory, General Electric Co.—The determination of the orientation of a single crystal requires a new type of apparatus. The crystal is mounted so that it may be rocked back and forth through an angle of about 45°. The surface to be examined is mounted at some predetermined angle χ to the direction of a beam of monochromatic x-rays when the crystal holder is at one end of its oscillation. The crystal holder carries a photographic film on a cylindrical holder whose axis is the axis of rotation of the crystal so that the film rotates through the same angle as the crystal. Behind this film is a stationary cylindrical film mounted in the usual way. This stationary film serves to identify the reflecting crystal planes, for it receives a diffraction pattern of the ordinary type which is measured in terms of the total angle of deviation of the beam. This angle is twice the grazing angle θ. Measurements on the rotating film give the angular rotation ρ at the instant of reflection. $\rho = \theta + \chi + \varphi$ where φ is the angle between the surface of the specimen and the plane which causes the reflection. The angles χ and φ may be either positive or negative depending upon experimental conditions.

14. The universal applicability of x-ray doublet laws in the field of optics. I. S. BOWEN and R. A. MILLIKAN, California Institute of Technology.—The relativity doublet formula is found to predict exactly the p, d, and f term doublet-separations in the succession of similar atomic structures Li(I), Be(II), B(III), C(IV), N(V); also in

Na(I), Mg(II), Al(III), Si(IV), P(V), S(VI); also in B(I), C(II), N(III), O(IV); also in Al(I), Si(II), P(III); also in Be(I), B(II), C(III), N(IV), O(V); also in N(II) and O(III); also in Mg(I), Al(II), Si(III), P(IV). All of these types of ionization have been definitely found in "hot-spark" spectra. The Hertz irregular doublet law has been found to predict the difference between the s and p terms and the p and d terms in optical spectra.

15. Difficulties with the Bohr atom. R. A. MILLIKAN and I. S. BOWEN, California Institute of Technology.—Our experimental work reported in the preceding paper constitutes an interesting step in the direction of the simplification of our working formulas; it makes possible a definite correlation throughout of x-ray and optical levels; it also brings about complete uniformity in the assignment, hitherto usually contradictory, of inner and azimuthal quantum numbers in these two fields. On the other hand it appears to require either the abandonment of the relativity explanation of the regular doublet, or else the abandonment of the familiar assignment of the s, p, d, f, etc. terms to the azimuthal quantum numbers 1, 2, 3, 4, etc., respectively.

16. Quantum defect and atomic number. LOUIS A. TURNER, Princeton University.—The square root of the quotient of the Rydberg constant and a term value gives the effective quantum number. Subtracting this from the true quantum number gives the quantum defect. This approaches a limiting value for the higher terms. It is found that this limiting quantum defect is a linear function of the atomic number for corresponding series, for elements of the same chemical sub-group, provided Bohr's quantum numbers be increased for elements of atomic number above 28. The quantum numbers for the normal orbits in Rb and Cs are taken to be 6_1 and 8_1, respectively, and similar changes made in all of Bohr's numbers. The slopes of the lines are all nearly the same. These relations apply only to series corresponding to penetrating orbits. The s lines of elements of different chemical nature and spectral type lie close together, indicating that the quantum defect depends primarily upon atomic number and secondarily upon particular atomic structure. The p lines for all neutral elements lie approximately 0.50 below the s lines. The quantum defects for ionized atoms are less than those of the corresponding neutral atoms and the $s-p$ difference is less, the higher the degree of ionization.

17. Soft x-ray levels and the Bohr scheme of atomic structure. F. L. MOHLER, Bureau of Standards.—A wide range of published data on critical radiation potentials of solids and gases has been used to trace the energy levels of atoms from the optical to the x-ray range. The results are in general consistent with the conclusions of Bohr and Coster as to the probable course of soft x-ray levels on the Moseley diagram. Some of the critical potentials evidently measure excitation without ionization, but contrary to the views of Rollefson and McLennan there is some evidence that most of the more prominent critical potentials measure ionization potentials.

18. Fine analysis of the Stark effect for Hβ and He λ4686. J. STUART FOSTER, National Research Fellow, Yale University.—Seven of the components which Stark has recorded for Hβ at 104 kv/cm are not predicted by the theory. The purpose of the present investigation was to see if some of these were grating ghosts as has been commonly assumed. Many photographs taken by Lo Surdo's method show all components observed by Stark which agree with the theory, and no others. On the other hand, one photograph of the parallel components alone shows Stark's components ± 4 with even greater relative intensity than he has assigned to them. As an explanation, the writer suggests that the spurious components are produced by variations in the direction of the applied field. Thus it is believed that a part of the energy of a real perpendicular component must produce on the plate an apparent parallel component, and vice versa. This explanation is supported by accompanying analyses of He λλ4922, 4472;

and by variations in the pit formed in the cathode. The photographs also show a fine analysis of the ionized helium line λ4686 of the predicted type, but somewhat obscured by other lines. At 33 kv/cm the strong outside parallel components have a separation in excellent agreement with Epstein's theory. At 46 kv/cm the displacements of the two perpendicular components on the red side are 0.37 and 0.76 A; the calculated values are 0.33 and 0.66 A.

19. Chlorine spectrum in the extreme ultraviolet. J. J. HOPFIELD, University of California.—In this preliminary work on the ultra-violet spectrum of chlorine, when the dry gas is used to fill both the receiver and the discharge tube of the vacuum-grating spectrograph, its spectrum is found to extend to λ790, and hence the gas is not too opaque for spectrum analysis in this region. Many new strong lines have been observed and others were obtained which check with those found by Millikan using the vacuum spark method. Some of the groups of lines, on comparison with similar groups in the new sulphur spectrum (Nature **112**, 437, 1923), give strong evidence that those lines in the arc spectrum of sulphur which have not yet been classified into the series of sulphur are in reality arc lines, and that these found in chlorine are consequently Cl(II) lines. When aluminum electrodes were used, a condensed discharge brought out the aluminum lines first observed by Lyman and only recently classified into spark series by Paschen. (Lyman, Spectroscopy; Paschen, Ann. der Phys. **71**, 152, 1923.) One of the most marked features of the spectrograms is a new group of *bands of aluminum chloride* that occurs at λ2620.

20. The vacuum spark spectrum of zinc in the region λ2100-4000. R. A. SAWYER and E. J. MARTIN, University of Michigan.—The vacuum spark spectrum of zinc has been investigated with a large quartz spectrograph. The spark box was constructed of Pyrex glass. The electrodes were mounted on heavy tungsten leads which were sealed into tubes that turned in ground joints so as to permit adjustment while sparking. A high vacuum and the glass insulation permitted the use of a very violent, condensed spark. Of the arc spectrum only the subordinate triplets $2p-3s$, $2p-3d$, and $2p-4d$ appeared with considerable intensities. All the other arc lines were weak or absent. All the spark lines given by Exner and Haschek appeared. In addition about 250 new wave-lengths have been recorded. About 100 of these were among the strongest lines in the spectra and have been measured on three or more plates. The new lines were grouped to some extent in the regions λ2400-2700 and λ3500-4000. As yet no additional lines have appeared in the region λ2000-2200 although the known lines in this region were strongly recorded. The work is being extended into the visible region.

21. The infra-red line spectra of zinc and cadmium. H. M. RANDALL and W. N. ST. PETER, University of Michigan.—In the work described the authors give the results of their investigations of the spectra of zinc and cadmium in the region between 1μ and 5μ. The arrangement and methods in this work are similar to those employed by Randall and Barker in 1919 with the following modifications. The source was an open carbon arc with 100 amperes capacity at 220 volts, the metals under investigation being inserted in the cored positive electrode. The diffraction grating was of the echellette type and was made by Barker at the University of Michigan. This grating has 7200 lines to the inch and is ruled so as to have its maximum energy in the region around 2.5μ. The effectiveness of this type of grating has been demonstrated. A list of new lines is given. Most of these have been identified by means of the combination principle with an accuracy of 5 A or less. Graphs indicating the changes in energy levels are included.

22. The spectrum of "nebulium." HARVEY B. LEMON, University of Chicago.—The spectra of the nebulae as summarized by Wright (Lick Observatory Publications, Vol. 13, 1918) contain 70 lines, which include, in addition to the lines of hydrogen,

helium, and ionized helium, 35 lines of unknown origin. These, together with 11 others not included in Wright's paper, and with the exception of one line whose identification as distinct from a helium line is uncertain, have been found to lie within the accuracy of measurement upon five branches of a parabola in which an index number is plotted as ordinate against wave numbers as abscissa. These parabolas open toward the red, and all have axes of approximately the same small inclination to the wave number axis. Of very great significance also may be the fact that 13 lines of ionized helium out of a total of 18 lie somewhat irregularly distributed on the same curve, and that the lower branches of all five curves by large extrapolation may intersect in the vicinity of the position of the first line $H\alpha'$ of the spectrum of ionized helium, λ10,126.6 A. The formulation was first made on the basis of the 35 lines given by Wright. The 11 others, on which information was subsequently obtained, were found to be taken care of on the same curves; and this is the chief reason why these results are thought to be of considerable significance.

23. An apparently new spectrum associated with spectra of unknown origin in the tails of certain comets. HARVEY B. LEMON, University of Chicago.—The tails of comets Daniell and Morehouse have been found to show band spectra of unknown origin not occurring generally in cometary nuclei, and these spectra have been reproduced in the laboratory by Fowler and by Merton, who attribute them, we believe quite properly, to carbon or some of its compounds. Merton has found that the presence of helium greatly facilitates their production. The new spectrum, which is the subject of this paper, lies in the ultra-violet region and could, therefore, never be observed in comets' tails directly. It never fails to make its appearance under a wide variety of conditions, all of which bring out the visible comet tail bands. The bands of which this spectrum is composed possess an unusually simple structure, and they have been produced with sufficient intensity to enable a photographic record to be made in the second order of a 21-foot Rowland concave grating. Because of the simplicity of their structure, it is hoped that an analysis along the lines of the present quantum theory of band spectra will yield important information as to the nature of the radiating molecule.

24. The line spectra of W and Ni in the afterglow of a discharge through a mixture of N_2 and A. A. G. WORTHING and R. RUDY, Nela Research Laboratory.—In a discharge through 99.8 per cent A+0.2 per cent N_2 at a pressure of 300 mm, two afterglows were obtained. With tungsten electrodes, one afterglow was orange colored. Its spectrum showed strongly the first and second groups of positive nitrogen bands. The other afterglow was blue. Its spectrum showed strongly the tungsten lines superposed on a faint background consisting of a continuous spectrum and of nitrogen bands. Both afterglows were obtained either separately or simultaneously. Low electrode temperatures and quiet discharges favor the first type. High electrode temperatures and condensed discharges with series spark gap favor the second type. In the latter case, a dark deposit probably a tungsten nitride forms on leads and glass container. With nickel electrodes the blue afterglow changed to green showing strong nickel lines. This is believed to be the first record of the excitation of the line spectrum of a highly refractory element by active nitrogen. The afterglows obtained from the argon nitrogen mixture were far stronger than those obtained in nitrogen only. No argon lines were seen during the discharge or in the afterglow.

25. The excitation of the spectra of the copper halides by active nitrogen, and the application of the isotope effect to the interpretation of band spectra. ROBERT S. MULLIKEN, Harvard University.—Active nitrogen was used to excite the spectra of CuCl, CuBr, and CuI. Probably an excited nitrogen molecule on collision with a CuX molecule either (1) excites a copper electron which in CuX_2 would act as a valence electron (result, emission of CuX bands), or (2) dissociates the molecule and excites the copper

atom (result, emission of copper arc lines), or (3) forms copper nitride (shown by chemical tests, although apparently no spectrum results). Examination of the CuX bands reveals the expected vibrational isotope effect in all three halides. With this effect as a guide, each spectrum proves to consist of several partly superposed band-systems. The heads of the green CuI bands are given ($n'=0,1.....8$; $n=0,1.....12$) by: $Cu^{63}I$, $\nu=19{,}708.3+211.9n'-2.35n'^2-264.5n+0.69n^2$; $Cu^{65}I$, $19{,}708.3+209.7n'-2.30n'^2-261.8n+0.68n^2$. These bands have a characteristic intensity distribution probably typical of the band spectra of many salts, and such as might be expected for an inharmonic oscillator.

26. The band spectrum of water-vapor. WILLIAM W. WATSON, University of Chicago.—Results both of an experimental and theoretical nature lead to the conclusion that the ultra-violet water-vapor bands have their origin in the hydroxyl ion rather than the water molecule. For both hydrogen and oxygen are necessary for their production, and it is impossible to excite this spectrum with the weakest electrodeless discharge through flowing water-vapor without causing the appearance of the Balmer hydrogen lines, thus indicating that the H_2O is easily decomposed into OH and H. Furthermore, the application of the quantum theory of band spectra to the fine structure of the λ2811 and λ3064 bands gives information favoring OH as the carrier. The λ2811 band has been photographed with high dispersion and every line has been assigned to a parabolic series. Departures of the relationships between the lines of these bands from the predictions of the simple quantum theory of band spectra have been found. The moment of inertia of the molecule is not a constant quantity, but varies with its speed of rotation. Two types of OH molecules appear to exist; one with but seven electrons, the other with the full complement of eight electrons.

27. The band spectrum of mercury and the dissociation of hydrogen by excited mercury atoms. K. T. COMPTON and LOUIS A. TURNER, Princeton University.—We have found that the band spectrum of mercury, the three strongest bands of which are of wave-lengths 4219, 4017, and 3728, appears strongly in the striated positive column of a hot cathode Geissler discharge in a mixture of hydrogen and mercury vapor, disappears when the hydrogen is pumped out, and is roughly proportional in intensity to the amount of hydrogen present. This indicates that the spectrum is emitted by a mercury hydride, in confirmation of the predictions of Kratzer and of Mulliken based on a study of the line structure of the bands from the point of view of the quantum theory. The emission is strongest in those parts of the discharge where other experiments indicate the highest concentration of excited mercury atoms. Apparently this spectrum results from an action of excited mercury atoms and not from the excitation of already existent hydride molecules. We suggest the hypothesis that the excited mercury atom reacts with a hydrogen molecule to form both a hydrogen atom and an excited hydride molecule which then emits the band spectrum, rather than simply dissociating the hydrogen molecule, as suggested by Cario and Franck. Our explanation meets fewer difficulties in the consideration of thermal equilibrium.

28. A band of unusual structure probably due to a highly unstable calcium hydride molecule. ROBERT S. MULLIKEN, Harvard University.—In the calcium arc in hydrogen at low pressure, an isolated band occurs in association with the lines of neutral calcium. Thus it is probably due to a compound of an excited (not ionized) calcium atom. The wide spacing of the lines and absence of appreciable isotope effect practically assure its hydride origin. The simple structure indicates a diatomic molecule. The lines of the two branches can be represented by the formula (obtained by term isolation), $\nu=28{,}358.43\pm2.365-2.311\ m\pm9.603\ m+0.566m^2\mp0.00342m^3-0.000662m^4$, where $m=\frac{1}{2}, 1\frac{1}{2},....9\frac{1}{2}$ for the positive branch (upper signs) and $1\frac{1}{2}, 2\frac{1}{2},.....11\frac{1}{2}$ for the negative. (Formulas with integral quantum numbers are also possible.) The lines

$m_{pos.}=9\frac{1}{2}$ and $m_{neg.}=11\frac{1}{2}$, which should both correspond to $m'=10\frac{1}{2}$ ($10\frac{1}{2}$ quanta of rotation in the *initial* electronic state of the molecule), are, however, both displaced by -0.62 units; and after this there are *no more lines* in either branch. The obvious and most probable explanation is that the molecules in the excited state begin to expand rapidly by centrifugal force (the extraordinarily high coefficients of m^3 and m^4 in the formula also indicate such a tendency) near $m'=10\frac{1}{2}$, and cannot exist with higher values of m'.

29. The 23 volt arc in helium. C. B. BAZZONI and J. T. LAY, University of Pennsylvania.—New and satisfactory photographs with and without neutral tinted wedges have been taken in mercury free helium at 23 volts and at 26 volts, i. e. below and above the normal ionization point. A hollow nickel anode is used. A non-inductive series resistance of 10,000 ohms is introduced to prevent oscillations and the consequent production of undetected voltages. The 23 volt spectrum is markedly different in appearance from that taken at 26 volts with the same bombarding current. Although at 23 volts crossed orbit lines of the lower order numbers are present, especially 5016 which is strong, the coplanar lines are notably more conspicuous. It is a fair statement of the facts to say that the 23 volt arc is predominantly coplanar.

30. Theory of normal and abnormal low voltage arcs. K. T. COMPTON and CARL ECKART, Princeton University.—A continuation of the study of the "abnormal" low voltage arc (one in which current and voltage are oscillating) which was described at the preceding meeting of the Society has led to a fairly complete physical interpretation of the phenomena there described, including the oscillations observed under certain conditions. The arc current i and voltage V must satisfy two conditions. The first, imposed by the external circuit, is given by $V=E-Ri$, where R is the series resistance and E the impressed e.m.f. The second depends upon internal characteristics of the tube, involving space charge, critical potentials of the gas, filament saturation current and geometrical features. These latter conditions are given at various stages of current as E is increased (1) when V is less than the minimum radiating potential V_r; (2) when V exceeds V_r but is less than the ionizing potential V_i; (3) when V exceeds V_i. It is shown that the nature of cumulative and direct ionizations causes a discontinuous decrease in V and increase in i at some voltage greater than V_r. Oscillations set in when the space charge around the filament becomes positive and the increase of current to saturation value causes the voltage to drop below V_r, thus again diminishing the current, and so on. This interpretation is supported by spectroscopic evidence, observations on the heating of the filament, and considerations based on the life of excited atoms.

31. Absorption of helium radiation by helium. A. LL. HUGHES and F. E. POINDEXTER. Washington University.—Helium radiation was excited by bombarding helium atoms by electrons of a definite velocity. The radiation fell upon a nickel plate 30 cm away, in the same vacuum, and produced a photo-electric effect which was measured by an electrometer. If the energy radiated is proportional to the number of impacts between the electrons and atoms, then the photo-electric effect should be proportional to the number of impacts provided that there is no absorption. Assuming that the deviation from proportionality is due to absorption, the absorption coefficient can be calculated. The numerical value of the absorption coefficient β in the exponential factor $e^{-\beta pd}$ refers to 1 cm distance and 1 mm pressure. For radiation excited by electrons of 22.8 volts energy, the maximum value of β was about 6.5 and decreased with increasing pressure, suggesting that the radiation was heterogeneous so that the more absorbable radiation was filtered out first. For radiation excited by electrons of 26.8 volts energy, the maximum value of β was about 2.5. For radiation excited by 91 volts, the absorption could not be detected by this method within the range of pressures used (.001 to .018 mm).

32. Critical potentials and spectra of arsenic, antimony and bismuth. ARTHUR E. RUARK, F. L. MOHLER, P. D. FOOTE, and ROY L. CHENAULT, Bureau of Standards.—The Bi lines 3067, 2276, 2230, 2228 and 1954 A were photographed in absorption. Below 1000°C As and Sb give only band and continuous absorption. Bi has groups of absorption bands between 2874 and 2672 A and below 2205 A. Foote, Rognley, and Mohler measured the critical potentials of these elements, but data were published only for As. The voltages of inelastic collision and ionization are: As, 4.7 and 11.5; Sb, 1.7 ± 0.5 and 8.5 ± 1; Bi, 2.0 and 8.0. We photographed thermionic discharges in Bi at potentials from 4 to 60 volts. Spark spectra appeared at 14 ± 1, 25 ± 5, and possibly at 45 ± 5 volts. The resonance potential corresponds to several weak lines. The raies ultimes 3067 and 4722 A appear at 4 volts. The critical potentials of the other elements are apparently related to the atomic spectra. The arc spectra are characterized by doublets. The lowest orbits in As are of *d*-type; in the other elements their character is unsettled. In each element the lowest orbits form a compact group well separated from all others. Some bismuth lines have fine structures which will probably require the introduction of a new quantum number, called the fine quantum number.

33. Intensities in the argon spectrum. PERCY LOWE and D. C. ROSE, Queen's University, Canada (introduced by A. Ll. Hughes).—A quantitative measurement has been made of the variation in the intensity of 50 argon lines, excited by electronic impact, as the energy of the exciting electrons varied from 24 to 140 volts. The apparatus consisted of a large three-electrode tube through which pure argon was continually passed at a constant low pressure. A constant current was maintained between filament and plate; the grid and plate were kept at the same potential, and the spectrum of the gas in the field-free space between these photographed. For measuring intensities, the neutral wedge method was used. The results show a division of the argon lines into two main classes corresponding in general to the red and blue spectra. Those in the latter class first appear at slightly over 40 volts, increase rapidly to a maximum at about 65 volts, then decrease slightly and remain fairly constant at higher voltages. The lines of the red spectrum are subdivided into two groups in one of which the intensity decreases steadily above 30 volts while in the other, after small variations at low voltages, it remains practically constant. This work was carried out by means of a grant from the Honorary Advisory Council of Canada.

34. The application of ultra-violet photographic photometry to problems of atomic structure. GEORGE R. HARRISON, National Research Fellow, Harvard University.—Applications of the correspondence principle emphasize the need for more exact methods of determining light intensities. The present work is an attempt to determine the variation with wave-length of the series limit absorption in alkali metal vapors, and to analyze isotopes quantitatively through their band spectra. The method used is generally applicable and increases the accuracy of measurements in the region 2100-5000 A. Little being known of the characteristics of photographic emulsions exposed to light below 3500 A, curves are being determined giving the variation of density with wave-length, time of exposure, and light intensity in numerous standard emulsions. Three-dimensional "characteristic surfaces" show the features of each emulsion in regard to sensitivity, contrast, scale, and obedience to the numerous suggested photographic laws. An electric absorption furnace is an integral part of the sensitometer. Twenty-two complete spectra are photographed on one plate, giving several values for each point and minimizing emulsion irregularities. A rotating disk spark gap of cadmium furnishes a steady source, intensity being controlled by a thermopile and carefully calibrated screens of wire mesh. Results are given in numerous curves and tables.

35. Note on the quenching of the fluorescent radiation in mercury vapor. JOHN T. TATE, University of Minnesota.—It has recently been suggested by G. Mie that atoms not only remain in the excited state for a mean time τ but also take a finite time to pass

from the excited to the normal state. He suggests the possibility that the energy J of the excited atom decreases exponentially during radiation according to the relation $J=J_0e^{-t/\tau'}$ where τ' may be called the transition time. It is further assumed that atomic collisions may de-excite the atom both before and during the radiation process. Applying these assumptions to the fluorescence of a gas it may readily be shown that the ratio R of the fluorescent to the incident radiation intensity is given by (1) $R=1/(1+\tau/T)\,(1+\tau'/T')$ where T and T' are the mean times between de-exciting collisions for the excited but non-radiating atoms and for the radiating atoms respectively. If, as Cario assumed, the act of radiation is instantaneous ($\tau'=0$) this becomes (2) $R=1/(1+\tau/T)$. This expression differs from the one derived by Cario. The experimental results of Wood and of Cario on the quenching of the fluorescent radiation from mercury vapor by the addition of foreign gases satisfy within the probable error an expression of type (2). Indeed they show that if we assume (1) then either τ/T or τ'/T' is a very small fraction, of the order of .01, of the other.

36. The luminous efficiency of chemi-luminescent reactions. ELLIOT Q. ADAMS, Nela Research Laboratory.—The efficiency of light production by chemical reactions proceeding at ordinary temperatures appears not to have been measured hitherto. Such a measurement was made in the case of phosphorus by saturating a stream of specially purified (atmospheric) nitrogen with phosphorus by bubbling through saturated solutions of phosphorus in refined cottonseed oil with finely divided phosphorus in suspension, and allowing the saturated gas to escape into the air. The intensity of the "flame" was matched by illuminating an annulus of filter paper with a miniature lamp bulb, sliding on a vertical rod. Approximate color match was secured by a suitable green light-filter. The data of Centnerszwer on the vapor pressure of phosphorus, together with the heat of combustion of phosphorus and the rate of flow of nitrogen, gave the energy input. The ratio of light production to energy input was found to be slightly more than one lumen per kilowatt, and not to differ materially at 25° and at 40°. Preliminary measurements of a similar kind have been made for the luminescence accompanying the oxidation of pyrogallol by hydrogen peroxide. Similar measurements will be made for other photogenic reactions.

37. The wave-lengths of fading and of absorption of the alkali chlorides colored by x-rays. P. L. BAYLEY, Cornell University.—Halite and sylvite colored by x-rays have strong absorption bands with maxima at .46μ and .55μ respectively (Phys. Rev. **21**, 716, 1923). The *color absorption* (absorption of the uncolored material minus the absorption of the colored material) of halite begins at 0.3μ and extends to 1.3μ. Placed in the spectrum, such substances fade over a very narrow region at first but the region spreads quickly to fairly definite boundaries beyond which fading can not be observed even after exposures 100 times those necessary to completely fade the first region. For four alkali chlorides, the regions of most rapid fading are: NaCl, 0.50μ; KCl, 0.61μ; CsCl, 0.63μ; and RbCl, 0.68μ. For NaCl and KCl these regions are shifted to the long wave-length side of the peaks of the color absorption curves of halite and sylvite because of the greater energy in the red end of the spectrum used. The curve given by the product of the ordinates of the incident energy curve (calculated) and of the color absorption curve of the material has a maximum at .500μ for halite and at .595μ for sylvite, which wave-lengths are nearly those of most rapid fading. Thus it seems probable that such materials are faded by the energy gained by their color absorption alone.

38. The problem of gas-opacity. JOHN Q. STEWART, Princeton University Observatory.—A survey of the general problem of gas-opacity is made, including a unified treatment of the subject, with references to the important researches dealing with dispersion, Rayleigh scattering, "resonance" scattering and selective absorption, the opacity of an ionized gas, and the transmission of radiation through a gas. The value of classica

electromagnetic theory in the treatment of these problems is discussed; and the tentative attempts which have been made to bring these matters under the quantum theory are indicated. (The study of opacity is related to the calculation of *intensities* of emission lines; to date the chief developments of quantum theory, and the greatest accumulations of experimental data, have been, however, in connection with *wave-lengths*.) The principles formulated are applied to certain astrophysical problems.

39. Note on the electromagnetic theory of radiation pressure. W. F. G. SWANN, University of Chicago.—The paper comprises a modification of the usual derivation of the expression for radiation pressure. It proceeds from the stand-point that the total value of $\rho(E+[VH]/c)$ integrated over the absorbing or reflecting plate is zero at all times. It is made for a fixed plate, and for a plate free to move, and its object is the removal of certain logical imperfections arising, in the usual derivations, from an attempt to consider, in addition to the primary beam, only those portions of the field generated by the motions of the electrons in the plate which ultimately cooperate to produce the reflected wave in the case of a reflecting plate, or the wave of cancellation in the case of an absorbing plate.

40. Free electrons in black body radiation. G. BREIT, University of Minnesota.—It is claimed by Pauli (Zeit. f. Phys. **18,** 273, 1923) that the work of Lorentz (Report of Solv. Cong., 1911) and of Fokker (Dissert. Leiden 1913; Arch. Néerl. (3a) **4,** 379, 1918) proves that the interaction between free electrons and black body radiation is of a non-classical nature and that therefore some such theory as Compton's for the interaction must be used. An examination of the problem shows, however, that the *observable* effects of the motions of electrons are consistent with classical electrodynamics provided the radiation satisfies Einstein's condition for the fluctuation of energy. The observable radiation pressure effects give the electron the classical value of kinetic energy. The rapid vibratory motions have a non-classical kinetic energy. These motions, however, are not observed and are not the motions treated by Fokker.

41. An optical effect of electrostatic charge. A. DE FOREST PALMER, Brown University.—The phase change, produced by negative electrostatic charge, in the elliptically polarized light reflected from a speculum metal mirror was measured with the strained glass elliptic analyzer described at the Chicago meeting in December, 1920 (Phys. Rev. **17,** 409, 1921). It was found to be proportional to the square of the surface density of the charge and to depend on the surface condition of the mirror. The surface of a freshly polished mirror changes so rapidly that the effect of an electric charge is masked by other phenomena. The results reported were obtained with a surface about two years old that showed no appreciable tarnish. This surface had reached a semi-stable state in which the changes were so slow that the relation between the electric effect and the angle of incidence could be approximately determined. The phase change per unit surface density was found to be $2.78\lambda\times10^{-5}$ at incidence 55°.8. It was zero at 68°.7, about one degree above the principal angle of incidence of the uncharged mirror, and passed through a minimum, $-2.4\lambda\times10^{-5}$, at about 80°. These results are in good agreement with a theoretical formula in the form $d=Af_1(\phi)-Bf_2(\phi)$ which shows that the effect also vanishes at normal incidence and at grazing incidence.

42. Explanation of the polarization experiment of Wood and Ellett on the classical theory. JOHN A. ELDRIDGE, University of Wisconsin.—Wood and Ellett have observed changes in the plane of polarization when a tube of mercury or sodium vapor which has been caused to fluoresce by polarized light is subjected to a magnetic field. The explanation of the phenomenon has not been clear. The results observed for mercury are shown to be in good agreement with classical electro-magnetic theory. According to Larmor's principle a magnetic field causes a precession of an electrical vibrator with angular velocity $\frac{1}{2}(e/m)(H/c)$, and to explain the present results we must hypothecate a time

of precession of about 3×10^{-7} seconds. This theory is substantially the same as that of the Zeeman effect. It is suggested that the differences observed by Wood and Ellett between the cases of mercury and of sodium are intimately connected with the differences which are known to exist in their Zeeman patterns. The results do not seem to be consistent with some of the tenets of the quantum theory.

43. Aberration of a ray of light, represented by a cone, in terms of theory of relativity (with demonstration of a geometric model). VLADIMIR KARAPETOFF, Cornell University.—An elliptical cone with two circular cross-sections is used. A generator represents the path of a particle moving at the velocity of light c. If the radii to the generator form angles δ and δ' with a reference plane, then one of the observers sees the ray at an angle δ, and another observer, moving at a relative velocity q, will see it at an angle δ'. The ellipticity of the cone depends on the angle α, where $\sin\alpha=q/c$. This leads to a novel expression for aberration, namely, $\tan\frac{1}{2}\delta/\tan\frac{1}{2}\delta'=\cos\gamma/\cos\gamma'$, where $2\gamma=90°+\alpha$ and $2\gamma'=90°-\alpha$. The observed ray is assumed to be in the XY plane and time T is used as the third dimension. The model is a generalization of the two-dimensional relativity model described by the author in Science and Invention, **11**, 442, 1923.

44. The normal and selective photo-electric effects in the alkali metals and their alloys one with another. HERBERT E. IVES and A. L. JOHNSRUD, Research Laboratories of the American Telephone and Telegraph Co. and the Western Electric Co., Inc.—The distinguishing characteristic of the selective photo-electric effect, exhibited in the liquid alloy of sodium and potassium, is an enormous enhancement of the emission under illumination at large angles of incidence for light polarized with the electric vector perpendicular to the surface. Occurring with this, in the case of sodium-potassium alloy, is a maximum in the spectral distribution of emission. Pohl and Pringsheim, finding spectral maxima of emission from rough surfaces of sodium, potassium and rubidium, concluded that those maxima proved the presence of the selective effect. Upon making mirror surfaces of potassium, by slow cooling of a pool of metal or by careful distillation on to an optical flat, the enhancement of emission at steep incidence is found to be absent; the ratio of photo-electric emissions for the two planes of polarization approximates the value two, which can be accounted for by the difference in optical absorption. Further experiments on mirrors of molten sodium, potassium, rubidium and caesium, show that the pure metals exhibit no selective effect. Of the alloys, only sodium-potassium shows selective characteristics.

45. Preliminary report on the variation of photo-electric effect with temperature. OTTO F. RITZMANN and W. R. HAM, Pennsylvania State College.—In order to test the effect of temperature on photo-electric currents at high temperatures a special tube was made consisting of a Universal Coolidge x-ray tube with an extra cathode mounted on the side toward the face of the anticathode and at right angles to its axis. The cathodes are symmetrically placed with respect to the face of the target, and either one may give an electron discharge producing x-rays which striking the other cathode produce a photo-electric current. The temperature of this second cathode is controlled and measured through its filament current, and is in general below the temperature of thermionic emission. Direct current high potential having been applied to the tube, the electron current from one cathode is measured with a milliammeter and the photo-electric current from the other is measured with a galvanometer. Since the solid angle subtended is quite large, photo-electric currents of the order of 10^{-7} ampere are obtained. It is found that on raising the temperature of the photo-electric cathode from room temperature to about 1400°C the current increases a fraction of 1 per cent apparently depending on the impressed potential difference. Results can be duplicated on either cathode.

46. Constancy of total photo-current from sodium with temperature change 20°C to −190° C. ROBERT C. BURT, California Institute of Technology.—Photo-currents from the surfaces of alkali metals have in general shown considerable changes when the surfaces were reduced to liquid air temperatures. Whether these changes have been due to a real temperature effect or to the formation of foreign surface films upon cooling in liquid air has not been determined. By the use of exceptional precautions in evacuating and by coating the inside of highly exhausted bulbs with sodium driven through the walls by electrolysis, it has been found possible to obtain a surface so pure that the photo-currents remain altogether unchanged when the bulb is dipped in liquid air. Furthermore, these surfaces show no photo-electric fatigue. This makes it possible for the first time to find the electronic work-function (long wave-length limit or critical frequency) of the alkali metals.

47. Electron emission from composite surfaces. K. H. KINGDON, Research Laboratory, General Electric Co.—(1) The electron emission from a tungsten filament, a fraction θ of whose surface is covered with thorium, can be represented by $\log_e i_\theta = \log_e (A_\theta T^2) - b^\theta T$. Langmuir (Langmuir and Kingdon, Science *57*, 58, 1923) has shown that $b_\theta = (1-\theta)b_w + \theta b_{Th}$. Since $b_w = 52600$, and $b_{Th} = 31600$ degrees, θ can be found from b_θ. The values of A_θ may be represented by the empirical formula $A_\theta = [a_w{}^{(1-\theta)} + a^\theta{}_{Th} - 1]$ where $a_w = 60$ and $a_{Th} = 6$ and $A_0 = 1$ amp./cm^2 T^2. (2) In a vacuum tube containing a completely formed ($\theta = 1$) thoriated tungsten filament at 1400°K, and Cs as a "getter," the electron emission is increased four-fold by the admission of a little nitrogen. The increase is about the same with the tube at 25°C or −180°C, and is not caused by ionization of the N_2. The effect is due to N adsorbed on the filament, but it does not vary rapidly with the pressure of N_2. (3) Oxygen was supplied to a hot tungsten filament at various rates. Between 1500°K and 1680°K the electron emission increased from 9×10^{-14} to 2.8×10^{-10} amp./cm^2, and was independent of the rate of supply of O_2, showing that the filament was completely covered with O. In the formula $i = AT^2e^{-b/T}$ the constants were found to be $A = 5\times10^{11}$ amp./cm^2, and $b = 107{,}000$ degrees ($\phi = 9.2$ volts).

48. The application of the third law of thermodynamics to electron emission. WORTH H. RODEBUSH, University of Illinois.—Dushman attributes the failure of his equation for the electron emission from coated filaments to the absence of conditions necessary for the third law. It seems rather that the deviation is due to the neglect of the specific heat of the electron in the metal. The cases where he finds the actual emission lower than he expected are precisely the cases where the specific heat of the electron has a large positive value. The constant A can not be a universal constant, since, if it were, we should find no thermo-electric force. In the analogous case of the vapor pressure of a monatomic solid we can integrate the Debye equation and obtain $p = [\nu_0{}^3(2\pi m)^{3/2}/(kT)^{\frac{1}{2}}]e - \Delta H_0/RT + 3/2$ where ν_0 is the fundamental frequency of the solid and m the mass of the atom. The question of electron emission can be approached from the standpoint of kinetic theory but the difficulty here is to assign the number of "free" electrons per unit area of surface.

49. Effective radii of gas molecules. L. L. NETTLETON, University of Wisconsin.—An investigation has been made of the *ionizing power of electrons of different velocities*. The results are expressed as the apparent radius of a gas molecule, when this radius is defined as that of the average sphere about the molecular center, through which an electron must pass to ionize the molecule. Measurements made on hydrogen, air, and mercury vapor with electrons of velocities from 100 to 2500 volts, show a regular decrease of the effective molecular radius with increasing electron velocity. By reducing the results of other experiments on ionization of air to the same basis, it is shown that for electrons ranging in velocity from 10^8 to 2.5×10^{10} cm per sec., there is

a regular decrease in the effective molecular radius of air molecules which is in general agreement with Rutherford's conclusion that the ionization should be inversely proportional to the square root of the energy of the ionizing electrons.

50. Mechanism of ionization in gases. IRVING LANGMUIR and H. A. JONES, Research Laboratory, General Electric Co.—With 30 volts or more and currents of milliamperes from a hot cathode, gases at 10 to 1000 bars are so intensely ionized that, except within a thin positive ion sheath around the cathode, the whole gas is slightly more positive than the anode (if of large area). Electrons from a filament in the axis of a cylindrical collector are projected radially with a constant velocity determined by the potential of the anode (an end-plate). The volt-ampere characteristic of the collector gives data for the free-paths of the electrons and proves that with 100-volt electrons most of the ionization is not directly caused by the collisions of electrons with atoms but the primary step is the production of a highly excited (nearly 100-volt level) atom or ion which subsequently ionizes other atoms probably photo-electrically by short-wave ultraviolet radiation. About 65 per cent of collisions of 100-volt electrons with argon atoms cause the electrons to lose all their energy in the production of the excited atoms, and about 24 per cent of the collisions cause the electrons to lose 13-volt energy (6.7-volt with mercury vapor). Eldridge's conclusions regarding ionization of mercury vapor are confirmed and extended to argon and other gases.

51. Remarks on the theory of the electric arc. PAUL S. EPSTEIN, California Institute of Technology.—It has been pointed out by K. T. Compton that the conductivity of the gas forming an electric arc can be accounted for by its thermal ionization. If this gas is really in thermal equilibrium, the positive and negative charge densities must be distributed in it according to the laws $\rho_1=\rho_0 e^{-\beta V}$ and $\rho_2=-\rho_0 e^{\beta V}$, denoting by V the electric potential, by ρ_0 a constant, and writing for short $\beta=e/kT$ (e elementary charge, k Boltzmann's constant, T absolute temperature). In the one dimensional case this leads to the equation for the potential $d^2V/dx^2=2\rho_0 \sinh \beta V$, the solution of which is $Amp(\beta V/2)=(2\beta\rho_0)^{\frac{1}{2}}x$. This formula gives roughly the right distribution of potential. It seems probable that the underlying assumption of thermal equilibrium is correct with respect to the positive ions. With respect to the electrons it is doubtful, but it is easy to modify the theory so as to cover this possibility.

52. On electrical discharges in gases with special regard to so-called dark discharges. JOHN ZELENY, Yale University.—Dark discharges between metal electrodes in gases are said to exist which have voltage-current characteristics differing from those of glow discharges. The existence of such discharges is questioned because observations with pointed electrodes show that the luminosity of glow discharges can be followed down to a current of about 1×10^{-8} amperes where the light gradually becomes imperceptible, and that there is no sudden change in the current as the voltage is reduced such as would be expected if the discharge changes its character when the light disappears. A study of the early stages of a point discharge was made when the current due to the initial ions alone could be measured on a galvanometer. When ionization by collision begins, the increase of current with voltage is quite gradual for positive discharges but is very abrupt for negative discharges. Micro-photographs taken of the luminous effects accompanying glow discharges from points in air at atmospheric pressure show the main features of these discharges. A dark space in the negative glow at atmospheric pressure corresponds to the Faraday dark space in discharges at low pressures. In helium, the Crookes dark space is visible at atmospheric pressure.

53. Mechanism of the discharge in gases. J. J. WEIGLE, Research Laboratory, Westinghouse Elec. and Mfg. Co.—Calculations of the energy acquired by an ion along one mean free path show that when the distance between the electrodes is great in comparison with the mean free path, the energy necessary to maintain the discharg

is smaller than the energy required to ionize a molecule. The Clausius law of repartition of free paths must come into consideration and in this way Towsend obtained an equation for α, the number of ionizing collisions in 1 cm. The experimental values of the probability of an electron ionizing a molecule show that it is a function only of the total number of collisions, and not separately of the pressure of the gas or the distance between the electrodes. This result is another way of formulating the Paschen law, but the experimental curve shows a completely different shape than the curve calculated from $\alpha-\beta$, $e^{(\alpha-\beta)a}=0$, the Towsend expression of the Paschen law. A theoretical explanation of this fact will be given in a later paper.

54. Diffusion of ions in neon tubes. T. E. FOULKE and W. H. MCCURDY, Edison Lamp Works, Harrison, New Jersey (Introduced by Saul Dushman).—The discharge was studied by ionizing the gas at the cathode by means of an auxiliary electrode. Electrons were then drawn from this discharge through the tube to the anode. The volt-ampere characteristics of the anode circuit were determined as a function of auxiliary gap current and voltage, tube diameter and length, and gas pressure. The following results were obtained: (1) Below the first ionizing potential the anode current depends on the auxiliary gap current, pressure, and tube diameter, but little on the voltage. The currents as a rule exceed the space current obtainable in a good vacuum. (2) At multiples of the ionization potential the anode currents increase about tenfold, finally reaching an upper limit. The conclusions drawn are as follows: (1) The initial current is due to a diffusion of ionized gas from the cathode region. (2) The current that is conducted through the tube is generated in the cathode region and is essentially a pure electron current. (3) The effect of the ionization in the positive column is to neutralize the space charge of the electron current. (4) The excess ions formed recombine. (5) The Faraday dark space is found to be the distance in which the electrons gain ionizing velocity.

55. Exponential rise of discharge currents in neon. T. E. FOULKE, Edison Lamp Works, Harrison, New Jersey (Introduced by Saul Dushman).—Assuming inelastic collisions, Townsend has derived a relation between the maximum number of electrons N produced by collision from N_0 electrons originating at the cathode, of the form $N=N_0 e^{V/V_i e}$, where V is the anode voltage and V_i denotes the ionization potential. It has been shown by Hertz, Compton and others, that in monatomic gases, the collisions are elastic below certain critical potentials. In the case of neon this potential coincides with that required for ionization (21.7 volts). The experimental results in neon (with either a hot cathode or photo-electric source of electrons) can be expressed by the relation $N=N_0 e^{V/V_i-1}$. This equation may be derived on the basis of the following assumptions: (1) That the ionization in neon is due to single impact at 21.7 volts, (2) that the collisions are elastic up to this potential, and (3) that the ionization per electron is X/V_i ions per cm of path, where X is the potential gradient. This relation is valid until the space charge, due to positive ions, causes a redistribution of the field, and for pressures great enough to insure at least V/V_i ionizing collisions between the electrodes. According to the work of Compton and Holst, it would be expected that the relation $N=N_0 e^{V/V_i}$ holds for this case. The experimental data in neon, however, are not in agreement with this latter relation. Further work is being carried out on other gases.

56. Excited atoms in the striated glow discharge in mercury vapor. W. H. MCCURDY, LOUIS A. TURNER and K. T. COMPTON, Princeton University.—The first author has found that striations are possible only in the presence of slight impurities, that they occur at 5 volt intervals and that the current increases as impurities are removed. The interpretation suggested is that ionization in the striations is cumulative, depending on the existence of excited atoms, and that the action of impurities is to reduce the

concentration of excited atoms and prevent their diffusion into the dark spaces between striations. It is shown that mobility and space charge considerations explain the existence of striations only if diffusion of excited atoms is suppressed. To test this hypothesis, the spectrum of light from a separate mercury arc was photographed before and after passing through various regions in the positive column. Regions of glow were found to absorb all lines ending with $2p_{1,2,3}$ states, while dark regions did not thus absorb. The absorption became more prominent as the impurity was pumped out, being strongest in the uniform positive column. Conclusions: $2p_{1,2,3}$ excited atoms exist in large concentration in the striations but not in the dark spaces; impurities reduce these concentrations; the metastable states $2p_{1,3}$ are relatively most prominent; absorption involving inter-system transitions is less probable than that in one system.

57. Metastable states in low voltage mercury arcs. MILTON MARSHALL, University of Chicago.—Characteristic curves of alternating current arcs in mercury vapor were observed by means of a Braun tube oscillograph and showed analogous phenomena to those observed by Kannenstine in helium. With low frequency the arc struck between 12 and 20 volts depending on the pressure. By increasing the frequency a critical frequency could be found above which the arc struck at an applied voltage of about 3 volts. This frequency was constant over a considerable range of pressure but increased at low pressures. With various tubes and different degrees of purification this critical frequency ranged from 40 to 12 cycles. This time at which a low voltage will restrike the arc after it has been extinguished was verified by means of a commutator which short circuited the arc for 0.046 seconds and then applied the low striking voltage. The actual voltages required to cause ionization in the metastable products formed in the arc were obtained more exactly by intermittent arcs. Assuming 10.4 volts as the ionizing voltage for reference, the lowest ionizing voltage in the intermittent arc was approximately 5.0 volts. A second ionizing voltage was observed which was 0.8 volt higher. These figures agree with what would be expected for ionization of the $2p_1$ and $2p_3$ states, which from spectroscopic considerations should be metastable.

58. The energy of high velocity electrons. MARSH W. WHITE and W. R. HAM, Pennsylvania State College.—A determination of the heat generated by high velocity electrons at the molybdenum anode of an oil immersed and oil cooled Coolidge x-ray tube was made by noting the temperature rise of the oil. The current and voltage furnished to the tube by a high tension direct current source was kept constant and continuously measured by potentiometers. Such measurements indicate that the total energy of the electron stream converted into heat during a one hour period remains constant within about 0.1 per cent when the voltage is raised from 10 kv to 23 kv and the current proportionately reduced; furthermore the rates of heating are equal. The same potentiometers measured the current and voltage supplied to a heating coil immersed in the oil. The heat developed by this "low potential" source was the same, within about 0.1 per cent as that developed from the "high potential" electron stream for equal powers and times. Other data indicate that no heat is generated at the cathode. Hence, if the energy due to x-radiation is included, the rate at which heat is generated by the electron stream in an x-ray tube is given within 0.1 per cent by the product of current and voltage.

59. The deflection of an electron beam by an alternating electric field externally applied. L. T. JONES, University of California.—A constant electrostatic deflection of a cathode beam is obtained only by an internally applied electric field. A varying external electric field produces a varying deflection, the deflection being a maximum at the moment of greatest rate of change of the electric field. This may be peculiar to the single frequency thus far used (60 cycles a.c.). Ebert failed to obtain this 90° phase difference and attributed the deflection to an "effect of the glass" of the tube. Addi-

tional glass placed in the field alters neither phase nor magnitude of the deflection. It is difficult to reconcile J. J. Thomson's compensating layer of electrons, high electron mobility and a deflection, particularly a deflection of 90° phase, with the deflecting field. The phase and deflection are both readily explained on the basis of a magnetic effect of the varying electric field. The magnitude of the deflection is not readily explained, but is apparently a function of the intensity of the electron beam.

60. The mobility of actinium B in air. HENRY A. ERIKSON, University of Minnesota.—Air is drawn with a velocity of 2000 cm per sec. between two parallel plates, 4 cm apart, between which there is an electric field. The actinium B enters in a thin sheet of air at and parallel to one of the plates, and being positively charged, it is forced by the field to the opposite plate where it adheres to the surface at a point whose distance down stream depends upon its mobility in air, the air velocity and the potential gradient. The plate with the active deposit is removed, covered with another plate having a 5 mm slit at right angles to the plate, and is placed inside of an ionization chamber. The current due to the active deposit at the different down stream distances on the plate is then measured by means of a quadrant electrometer. It is found that the curve showing the relation between the current as ordinate and the down stream distance as abscissa has two maxima, one of which corresponds to a mobility in air of 3.15 cm/sec/volt/cm and the other to a mobility of 1.20. The interpretation of these results is not clear, but it is believed that at least the greater mobility value (3.15) is due to atomic actinium B. It is significant that the slowest of the above ions has a mobility of the same order as the final positive air ion (1.36), although its mass is much greater, and the other, though also of a much greater mass, has a mobility greater than either the initial positive or negative air ions (1.87). This signifies that, aside from the charge, it is the ionic volume rather than the ionic mass which determines the mobility.

61. A method for studying the ionization of the less volatile metals. K. H. KINGDON, Research Laboratories, General Electric Co.—When an atom strikes a hot surface whose electron emission work function ϕ is greater than the ionization potential V of the atom, an electron is taken from the atom by the surface, and the resulting positive ion evaporates. A hot tungsten filament will ionize any atom for which V is less than 4.5 volts. The method may be extended by the use of a tungsten filament covered with a monatomic layer of oxygen ($\phi=9.2$ volts). In this way ions of Cu ($V=7.69$), Bi ($V=8$), Ca ($V=6.1$) have been obtained, whereas Hg ($V=10.4$) does not show the effect. A little of the metal is vaporized on to the oxygen-covered surface. The latter is then suddenly heated to 1400°K and the evaporated ions observed by the kick of a ballistic galvanometer. Or the metal may be allowed to strike the hot filament at a steady rate, and the steady ion current measured. By evaporation of some of the oxygen, ϕ may be reduced to any value between 9.2 and 4.5, and by studying ion generation at these partially covered surfaces estimates of the ionization potentials of the metals can be made. (Cf. Kingdon and Langmuir, Phys. Rev. **21**, 380, 1923.)

62. The source of the penetrating radiation found in the earth's atmosphere. RUSSELL M. OTIS and R. A. MILLIKAN, California Institute of Technology.—Assuming, following Kolhorster's 1923 conclusions, a penetrating radiation of cosmic origin which produces 2 ions/cc/sec. at sea level and has an absorption coefficient per cm in water of 2.5×10^{-3}, we find that this radiation would produce 9 ions/cc/sec. on top of Pike's Peak (14100 ft). Inside our completely enclosing lead shield, 5 cm thick, it should produce 7.8 ions/cc/sec. The ionization in our apparatus contributed by the walls and the lead shield was found to be at least 7 ions/cc/sec., so that if there were no local radiation on Pike's Peak, the lowest obtainable value of the ionization in our shielded vessel should have been 14.8 ions/cc/sec. We observed as low as 11. We conclude, therefore, that there exists no such penetrating radiation as we have assumed. Second,

we found as a result of a snow-storm on the mountain as large a percentage change (about 10 per cent) in the ionization inside our 5 cm lead shield as outside it. We interpret this result also as meaning that the whole of the penetrating radiation is of local origin. How such quantities of radioactive material get into the upper air is as yet unknown.

63. Results of preliminary earth-current measurements at the Carnegie Institution's Magnetic Observatory near Watheroo, Western Australia. O. H. GISH, Department of Terrestrial Magnetism, Carnegie Institution of Washington.—The first continuous records of earth currents in the Southern Hemisphere were obtained in October 1923 on the recently constructed experimental lines at the Watheroo Magnetic Observatory. The method of measurement employed there is described in Terr. Mag. **28**, 89-108, Sept. 1923. The chief novel features are: (1) The use of five earthed points instead of the usual three, (2) provision for comparing the relative efficacy of aerial and subterranean connecting lines, and (3) the use of a multiple-point recording potentiometer. The preliminary results obtained in November and December 1923 seem to show that the method employed is very satisfactory and has some distinctive advantages. Both gradient components show a pronounced diurnal variation. The south-north, taken positive when directed northward, has a principal maximum at about 7 a. m., a principal minimum near noon, a secondary maximum at about 5 p. m., and a secondary minimum near midnight, results which are in qualitative agreement with the data from Berlin and Ebro. The east-west component, taken positive when directed westward, is however simpler in form, showing only a single period, with maximum at 9 or 10 p. m. and a minimum near 11 a. m.

64. Note on the theory of the single fiber electroscope. W. F. G. SWANN, University of Chicago.—If k is the mechanical restoring force per unit displacement of the fiber, the actual restoring force per unit displacement may readily be shown to be $k-CX^2$, where C is the capacity of the fiber and X the field between the plates. The deflecting force due to a change of potential δV in the fiber is $CX\delta V$, so that the sensitivity s is $s=CX/(k-CX^2)$. If k is less than CX^2 the instrument is unstable, and the fiber flies to either one plate or the other. The sensitivity becomes very large if $k-CX^2$ is small; and, in obtaining high sensitivity from the instrument, this condition is usually satisfied, even though the fact may not be realized. It is a bad condition since it results in large variations in s for small variations in either k or X. If we should desire to restrict ourselves to the case $k-CX^2=\frac{1}{2}k$, so that we draw upon the term CX^2 to the extent of no more than doubling the sensitivity which we should obtain in its absence, s reduces to the very simple expression $s=1/X$ which, under a magnification of 100 gives a deflection of 1000 mm per volt for a field of one volt per cm between the plates. High sensitivity consistent with great constancy *necessitates a small field* between the plates, and correspondingly small value of k. An instrument meeting the required conditions is described.

65. The Ampere trough experiment and its explanation by the usual electromagnetic laws. F. W. GROVER, J. P. DAS and J. TURNBULL, Union College.—In Jour. Franklin Inst. p. 559, Nov. 1921, Carl Hering describes a modification of the classical Ampere trough experiment for whose explanation he believes the usual electromagnetic laws inadequate. The present paper gives detailed experimental and mathematical analysis of this circuit. The circuit is a wire rectangle $ABCD$, 70 cm long, 25 cm wide, interrupted at the center of one long side CD by troughs of mercury, of rectangular cross section, 4 cm by 1 cm deep, perpendicular to CD and spaced 5 cm between centers. With the bridge close to CD on either side, there is no perceptible force. With the bridge inside the rectangle and 2 cm to 20 cm from CD, the force is away from CD. With the bridge inside the rectangle and more than 20 cm from CD, the force is *toward* CD.

With the bridge outside the rectangle and more than 2 cm from *CD*, the force is *away* from *CD*. If the length of conductor in the circuit be increased by movement of the bridge, an increase of inductance is possible even with a decrease of the area enclosed by the circuit. Calculation shows a maximum or minimum of inductance in regions where the direction of force changes. The bridge always moves so as to *increase* the inductance. Inductance measurements check the calculated values. Furthermore, analysis of the forces between the bridge and the other elements of the circuit by the usual laws explains the observed movements of the bridge. Recently published results of Morecroft, A.I.E.E., p. 1191, Nov. 1923, confirm these conclusions.

66. A method of measurement of cyclic changes of resistance. F. WENNER and F. M. SOULE, Bureau of Standards.—The method is a modification of that used by Schuster more than 50 years ago in his investigation of Ohm's law and by Perkins recently in his first investigation of the effect of charge upon conductivity of metallic conductors. In both of these investigations erroneous conclusions were drawn because of a similar error in the measurements. The modification made is such that only a negligible part of the test current passes through the galvanometer. This results in a very marked increase in both the sensitivity and in the reliability of the results obtained. Under favorable conditions cyclic changes in resistance can be detected with certainty when these amount to but 1 part in 10^8 of the resistance of the conductor in which they occur. This reliability may be obtained for pure metal conductors using a moving coil galvanometer and without control of the temperature. The method is suitable for frequencies from about 1 cycle per second upward to 10000 cycles per second or even higher. However, it is applicable only in those cases in which an alternating test current can be definitely synchronized with the cyclic changes in resistance.

67. The variation in the resistance of carbon and graphite with temperature. BRADFORD NOYES, JR., Cornell University.—(1) *Variation with temperature.* The resistance of *carbon* was found to decrease linearly with temperature. Several different specimens, made from braided silk, were observed from −190° to 2000°C. *Metallized filaments* showed a rapid decrease in resistance to about 400°C, when the coefficient changed. The resistance at 2000°C was found to be about twice the room temperature resistance. *Graphite*, made by the Acheson Company and purified by heating, behaved similarly to the metallized filament. A minimum in its resistance occurred about 600°C, the resistance above this point seeming almost a linear function of temperature. It was found that these experimental results do not fit either the law proposed by Bidwell, or that proposed by Waterman. (2) *Variation with air pressure.* Graphite, in the presence of air at about ¼ atmospheric pressure, was found to have resistance about 4 per cent lower at 500° than the same specimen had in a vacuum. This effect decreased with temperature, the resistance at room temperature being the same whether the specimen was in the air or vacuum. (3) At about 2200°C the length of carbon specimen was observed to increase, bending the specimen. This *increase in length* became permanent, and the bend remained even when the specimen was cooled.

68. An alternating current bridge for the measurement of the small phase angle of a high resistance. IRVING WOLFF, Cornell University.—An alternating current bridge has been developed for measuring capacities of the order of a microfarad to within a few percent when they are in series with 100,000 ohms or less. The action of the bridge depends on the addition of a fourth low resistance arm in addition to the usual Wagner arm. This makes possible a new method of adjustment of the Wagner arm which with the characteristics of the vacuum tube as detector allows the elimination of distributed capacity and inductance and earth capacity effects in the adjustable arms of the bridge and of earth capacity effects in the object to be measured. Tests made on known resistances and capacities have given satisfactory results.

69. Electrical resistance and thermo-electric power as a function of temperature. A. T. WATERMAN, Yale University.—In the writer's derivation (Phys. Rev. **22**, 3, 1923) of an expression for the free electron concentration within a conductor, the effect of the specific heat of electricity on the temperature variation of the ordinary electron evaporation constant was neglected in the usual manner. The inclusion of the specific heat term now improves the expression for the temperature variation of resistance already given, and also leads to a satisfactory equation for the thermo-electric power as a function of temperature. Thus taking the electron evaporation constant as $\psi=\psi_0+3/2kT-\int\epsilon\sigma dT$, and assuming $\sigma=\sigma_0 T$, the specific resistance becomes (1) $\rho=CT^a e^{b/T-cT}$ where (for unit valence) $a=1.25$, $b=(\phi_0-\psi_0)/2k$, $c=\epsilon\sigma_0/4k$. The thermo-electric power is (2) $Q=A+B/T+CT$, where $B=-(k/\epsilon)(b_2-b_1)$, and $C=(k/\epsilon)(c_2-c_1)$. For pure metals at ordinary temperatures the term B/T is small, and thus Eq. (2) very closely approximates the familiar linear form. The application of (1) and (2) to Bidwell's data (Phys. Rev. **23**, 3, 1924) for the alkali metals (where unit valence is essential) gives fair agreement both for thermo-electric power and temperature variation of resistance, in the solid state.

70. The significance of formulas for the inductance of a portion of a circuit. FREDERICK W. GROVER, Union College.—Since currents flow in closed circuits only, the concept of the inductance of an element of circuit can have practical significance only when defined with reference to its contribution toward the total inductance of the circuit. Thus self and mutual inductances of the elements of circuit should be defined so that the total inductance of the circuit can be obtained by summing contributions of the elements to the total. This agrees with common practice for a circuit composed of a number of mutually reactive coils joined in series. There is no essential difference between the mutual inductance of two isolated coils and that of two isolated straight wires. Accordingly, the mutual inductance of two straight wires AB and CD is defined including only that portion of the infinite number of flux linkages (unit current in AB) included between semi-infinite planes perpendicular to AB through the ends of CD. Flux linkages in question between CD and infinity are in the direction away from AB. Existing formulas for mutual inductance of wires agree with this definition. The objection urged against the use of the Biot-Savart law for deriving such formulas is rendered invalid by thus defining the inductance of an element with regard to the whole circuit.

71. An improved method for determining the dielectric constant of gases. C. T. ZAHN, Princeton University.—A modification of the use of high frequency oscillations for determining dielectric constants has been developed. Two generators produce in a detector-amplifier a heterodyne note which is adjusted by beats with a tuning fork. One generator is fixed; the other contains two capacities, C and K in series. C is the gas condenser; K, a large capacity with a small variable part. A small change in C, due to the gas, requires for compensation a large change in K given by $dK/dC=-(K/C)^2$, which can be made as large as desired. This is a null method and it depends in no way upon either the electron tube constants or the distributed capacity of coils unless these change erratically. The limit of accuracy depends then on the calibration of the condenser system and the steadiness of the circuits. It was found possible to detect with facility a dielectric constant given by $\epsilon-1=10^{-6}$, which corresponds to about one beat per second. Measurements were made on air, nitrogen, oxygen, and hydrogen.

72. The electric moment of gaseous HCl and HBr molecules. K. T. COMPTON and C. T. ZAHN, Princeton University.—By a method described in the preceding paper by one of the authors, measurements have been made of the dielectric constant of gaseous HCl and HBr throughout a temperature range of about 400°C beginning just above the liquefaction point. In order to prevent chemical action the condenser used was made of an alloy of gold with small quantities of platinum and palladium and

mounted in a Pyrex tube. Temperatures were measured to at least an accuracy of one-tenth degree by a platinum resistance thermometer wound around the condenser cylinder. The data obey accurately the Debye equation $(\epsilon-1)/(\epsilon+2)\rho=A+B/T$, based on the existence of fixed moments in the molecule. For HBr the moment is .7881 $\times 10^{-18}$ c.g.s.u. for HCl, 1.03×10^{-18} c.g.s.u. The latter value comes out about one-half the value given recently by Weigt and Falkenhagen and is about one-sixth the limiting value given for it by infra-red absorption data. It is therefore impossible to decide between Debye's classical theory and Pauli's quantum theory of dielectric constant by comparison of these experimental results with data calculated from infra-red absorption.

73. Potentials and Hertzian vectors for certain electromagnetic fields. H. BATEMAN and P. EHRENFEST, California Institute of Technology.—The field in which electric dipoles break up at the origin and radiate their constituents in opposite directions with velocity c, may be derived from a simple Hertzian vector involving the gradient of the logarithm of the ratio of $r+z$ to $r-z$. By operating on the field vectors with $\partial/\partial z+(1/c)\partial/\partial t$ the singularities radiated in one direction are eliminated. An operation $(1/c^2)\partial^2/\partial t^2-\partial^2/\partial z^2$, or the equivalent operation $\partial^2/\partial^2 x+\partial^2/\partial y^2$, eliminates both sets of radiated singularities and leaves the field of a fluctuating Hertzian dipole. The result of the last operation may be interpreted in terms of radiated pairs of quadrupoles and leads to a surprising conclusion.

74. Complete electromagnetic equations and a single system of units. GEORGE A. CAMPBELL, American Telephone and Telegraph Co.—The fundamental curl, wave, and activity equations are written: curl $H=GE+C\dot{E}=(\Gamma/K)E$;

$$-\text{curl}\,E=RH+L\dot{H}=(\Gamma K)H;\quad \Delta E=CL\ddot{E}+(RC+LG)\dot{E}+GRE=\Gamma^2E;$$

$$-\text{div}\,(E\times H)=d(\tfrac{1}{2}CE^2+\tfrac{1}{2}LH^2)/dt+GE^2+RH^2=(\Gamma/K)E^2+(\Gamma K)H^2;$$

$$\Gamma=[(R+ipL)(G+ipC)]^{\frac{1}{2}}=\text{propagation constant};$$

$$K=[(R+ipL)/(G+ipC)]^{\frac{1}{2}}=\text{iterative impedance};$$

where G, C, R and L are the conductance, capacity, hysteresis and inductance of a unit cube of the medium, which is the simplest unit into which the medium may be resolved. The discussion of any medium is thus made uniform with the ordinary discussion of any network since both are based on the values of G, C, R and L for the component units of the medium or network. It is urged that in all theoretical discussions of both media and networks the same units be employed as in actual physical measurements. The international metric and electric units considered as a meter-second-watt-ohm system are adapted for this purpose; the great numerical range required of a single system of basic units is conveniently obtained by using mega and micro numerical multiples (supplemented in special cases by kilo and milli multiples).

75. New researches on the magnetization of ferromagnetic substances by rotation and the nature of the elementary magnet. S. J. BARNETT and L. J. H. BARNETT, Carnegie Institution of Washington and California Institute of Technology.—In the last two years we have studied many rotors of soft iron, cold-rolled and annealed steel, nickel, cobalt, iron-cobalt, iron-nickel, cobalt-nickel, and Heusler's alloy. Great improvements have been made in the driving mechanism, in the compensating systems, in the construction of the rotors and rotor bearings, in the mounting of the magnetometer and methods of adjusting and testing it, and in the elimination of errors generally. The mean results do not differ greatly from the best of those we have published before; but the new results are more certain, precise, and extensive. The mean specific magnetic intensity of rotation λ (equal to the ratio of the angular momentum of the elementary magnet to its magnetic moment on the simplest classical hypothesis) is found to be close to $1.06\times m/e$. The average error for the individual rotors is about 1.2 per cent, and the average departure of λ for the individual rotors from the general mean is about 2.2 per cent. The above value is nearly a mean between the values obtained in the best

two determinations by the converse effect (Beck, Chattock and Bates) in iron and nickel. Classical theory requires $\lambda = 2m/e$; recent developments in quantum theory favor $\lambda = m/e$, but in comparatively simple cases.

76. Mechanical control of magnetization and of hysteresis in permalloy. O. E. BUCKLEY, Research Laboratories of the American Telephone and Telegraph Co. and Western Electric Co., Inc., New York.—*Nickel-iron alloys* containing 65 and 84 per cent of nickel show opposite effects of tension on magnetization. An alloy containing 81 per cent of nickel is nearly indifferent to tension. Incomplete annealing may completely mask the characteristic differences. Whenever magnetization is favored by tension the *hysteresis loss* is diminished. In an especially well-annealed alloy containing 78.5 per cent of nickel both effects are enormous, hysteresis in particular being reducible to about one hundredth of its amount in the best silicon steel. Residual hysteresis is so little that it is natural to regard it as evidence of slight inhomogeneity in the specimen rather than as an essential characteristic of the magnetizing process. The practically complete saturation of properly stressed wires in very weak magnetic fields taken in connection with x-ray photographs makes it very improbable that the equilibrium positions of the elementary magnets are connected in any way with crystal structures, except as the latter may introduce or modify stresses within the specimen.

77. A contribution to the theory of ferromagnetism. L. W. MCKEEHAN, Research Laboratories of the American Telephone and Telegraph Co. and Western Electric Co., Inc., New York.—The usual theories of ferromagnetism are inconsistent with modern views of atomic processes and are incapable of accounting for the magnetic properties of permalloy. A purely atomic quantum theory, as is pointed out, does not account for the magnetic hardness and hysteresis of ordinary materials. This defect is remedied by considering that the magnetization must proceed discontinuously in space as well as in time. This leads to the conclusion that atomic magnetostrictions, or rather the strains produced thereby, are the chief source of magnetic hardness in all cases. The abnormality of permalloy is explained as due to the fact that the atomic magnetostrictions in iron and nickel are of opposite types, so that in an alloy having the right proportion and distribution of the two elements, magnetostrictive strains due to either element are relieved by the magnetization of the other. The theory offers a reasonable explanation of the dependence of magnetic hardness upon mechanical hardness, and for the efficiency of annealing and quenching in altering magnetic quality.

78. On the temperature coefficient of frequency of quartz resonators. W. F. POWERS, Wesleyan University.—Provisional data obtained with crystals of 91 kilocycles frequency indicate that from 20°C to 110°C the frequency decreases by 0.0005 per cent of its value at 20°C for an increase in temperature of 1°C. Temperature coefficient of frequency is thus of the same order of magnitude as the thermal coefficient of linear expansion. A quartz slab 3 cm×0.5 cm×0.15 cm, approximately, is mounted between two brass plates 0.05 cm thick at a separation of 0.6 cm on a "Formica" base; clearance between brass plates and crystal is large enough to make the expansion effect of the crystal's mounting negligible. This system is heated in a furnace and connected to a non-regenerative tube circuit. To this is loosely coupled a generating circuit which is brought into resonance with the crystal at its different temperatures by the "key-tapping" method described by Prof. Cady (Proc. I. R. E. **10**, 109, 1922). A second crystal at constant temperature is used to determine variations in frequency of the generating circuit. The percentage probable error of a single comparison of frequency of the generating circuit with that of the crystal at constant temperature determined from 10 trials in quick succession is somewhat better than 0.001 per cent.

79. A method of producing a square wave of radio frequency. J. L. BOWMAN, University of Chicago (introduced by W. F. G. Swann).—A square wave of high frequency

is necessary in the measurement of electronic mobilities. The oscillations of a tube circuit A are rectified by a tube B and applied to the grid of a tube C in such a way that the grid is equal in potential to its filament during half the cycle and negative thereto during the other half. As a result, the potential difference between the ends of a resistance in the plate circuit of C suffers sudden increases and decreases between zero and a maximum value, remaining sensibly constant between these changes, thus giving rise to a square wave. The sharpness of the changes between zero and the maximum increases with increase of the amplitude of the voltage applied to the grid of tube B. This must not be too great for the safety of the tube. However, by suitably connecting the grid of tube B to tube A, through a battery, it is arranged that, after B has attained a potential of about 15 volts, the positive current leaving it becomes sufficiently great to insure that the upper half of its voltage-time curve is greatly flattened, thus avoiding a dangerously high voltage.

80. A preliminary report on the breath expulsion in singing with relation to pitch and intensity. DOUGLAS STANLEY and H. H. SHELDON, New York University.—The voices of various singers have been analyzed from the physiological and musical viewpoints with special reference to proper and improper tone phonations. These voices were then analyzed by physical means, regarding the voice merely as a sound-producing instrument. The physical analysis was made by a study of curves showing breath expulsion against intensity and breath expulsion against pitch. Over the head of the singer was strapped an air-tight mask in which was mounted a large tube opening into a spirometer and a telephone transmitter. This transmitter operated an oscillograph through a specially constructed three-stage amplifier. By these means intensity and breath expulsion were measured.

81. Some characteristics of a hot wire phonometer. ORIN TUGMAN, Riverbank Laboratories.—The resistance of a platinum wire mounted in a horizontal slit over a brass tube and heated by a current of electricity, is changed by a sound wave passing through the slit. In this experiment the change of resistance was measured by a potentiometer. The relation between intensity of sound and change of resistance was determined by mounting a calibrated telephone receiver over the apparatus and operating the receiver by a filtered current from a vacuum tube oscillator. For any given frequency a linear relation was found between the change of resistance and the square of the amplitude of the receiver diaphragm.

82. Sound intensity attenuation measurements on voice tubes. P. P. QUAYLE and E. A. ECKHARDT, Bureau of Standards.—The dissipation of sound energy along a voice tube transmission line is mathematically analogous to the dissipation of light in an absorbing medium and is therefore expressible by the equation $dI/dx = -\alpha I$. Measurements of the ratio of output to input intensities for voice tube lines which were progressively changed in length showed α to be constant within the errors of measurement and it may therefore be concluded that the equation adequately represents the intensity attenuation. The absorption constant α has been found to be greater for the higher pitches of the voice range than for the lower. Values for α have been determined for typical types of tubing. Design of a voice tube installation to give a predetermined intensity attenuation is therefore made possible. Difficulties due to resonant response of the tubing were minimized by using a sound source the frequency of which varied cyclically over a band of frequencies. The source of sound was a magnetophone supplied from an electron tube oscillator. By driving the rotor of an air condenser by means of a motor the oscillator frequency and hence the sound frequency was varied cyclically. This work was done in cooperation with the Navy Department.

83. Measurement of vibrations in building structures. F. R. WATSON, University of Illinois.—By means of a portable seismometer, patterned after the model described

by P. G. Nutting (A Portable Seismometer, Jour. Opt. Soc. of America, **6**, 629, 1922), vibrations of floors, table tops and other structures were magnified and photographed. The actual vibration of the structure was measured by noting with a microscope the motion of the seismometer mass. By these experiments, an analysis may be made that gives the frequency and amplitude of the component motions. It is also possible to measure the amplitudes of motion of partitions in comparison with the intensities of the sound given out.

84. Position finding in hydrography by a radio acoustic method. M. KEISER and E. A. ECKHARDT, Bureau of Standards.—The distance between two points is determinable by starting sound and radio signals at one and observing the time interval between their arrivals at the other. No appreciable error results in assuming the arrival and departure times of the radio signal to coincide. The distance is determined by multiplying the observed time by the sound velocity. A ship making depth soundings to be used in the preparation of hydrographic maps uses auxiliary shore stations. The ship is equipped for recording radio signals on a chronograph drum and for transmitting sound signals. At each shore station a hydrophone receives the sound signal and auxiliary apparatus provides for the automatic transmission of radio signals as a result thereof. The ship records the instant of firing a bomb as well as those at which the radio signals from the shore stations arrive. The travel times of the sound through the water from ship to each shore station are read from the chronograph chart. They are corrected for the lags which are currently determined. The combination of the computed distances gives the position of the ship on the chart. The operations of the ship are therefore independent of visibility. This work was done in cooperation with the U. S. Coast and Geodetic Survey.

85. The vapor pressure constant for silver. ROBERT J. PIERSOL, Research Laboratory, Westinghouse Elec. and Mfg. Co.—At higher temperatures, light reflection from polished silver surfaces changes rapidly from specular to diffuse due to evaporation. The rate of evaporation is determined at different temperatures by the loss in weight of silver filaments, 0.0051 cm in diameter and 10 cm in length. The vapor pressure of silver may be calculated using the kinetic relation, $m = p(M/2\pi RT)^{\frac{1}{2}}$. This data may be used to establish the constant for silver in the Hildebrand vapor pressure curve, $\log p = -3140\ C/T + 7.85 + \log C_1$ where C is the constant for silver. Calculation shows C to be 3.95. Von Wartenberg, using a dynamic method, gives the value of C as 4.30. On the other hand, Greenwood, observing the boiling points of silver at pressures of 0.14, 0.35 and 1.0 atmosphere, obtained results in agreement with 3.95 as the silver constant.

86. An electric furnace giving very uniform temperatures. WALTER P. WHITE, Geophysical Laboratory.—In precision work involving electric furnaces uniformity of furnace temperature in the majority of cases offers by far the most serious problem in the whole experiment. The furnace here described was of favorable dimensions, 2.7 cm wide and 25 cm long. Heaters in or across the ends, however, were not desirable. Two familiar devices were used: (1) The furnace tube which carried the winding was of silver 3 mm thick; (2) the end coils were separately regulated. Three features were new: (3) Alundum tubes 7 cm long continued the central silver tubes, affording thermal insulation at the ends. (4) The regulated end coils were wound on these tubes, thus diminishing the cooling effect of the ends. (5) The outer 6 cm at each end of the silver tube were occupied by 4 cup-shaped silver partitions in order to bring the wall temperature across the ends. By suitable regulation of the end heating coils the uniformity over the middle 14 cm was brought to 0.1° at 600°, or 0.2 per mille of the furnace temperature. When no current at all was used in the end coils, the maximum temperature difference within the 14 cm space was 7 per mille. It was about the same when the end coils were heated and no heat whatever was generated along the silver tube itself.

87. The molecular wedge theory of emulsions. WILLIAM D. HARKINS and ERNEST B. KEITH, University of Chicago.—An earlier paper (1917) indicated the shape of the soap molecules in the interface between water and oil to be important in the determination of the sizes of the drops in an emulsion, and whether the drops shall be of oil or of water. Finkle, Draper, and Hildebrand have found that the sizes of drops in emulsions produced by sodium, potassium, and caesium palmitate, are in accord with the theory. We find: (1) The curve for the distribution of the diameters of oil drops in an emulsion is similar to the Maxwell distribution curve for velocities. (2) The most probable size was found to be 4.7, 3.9, 2.9, and 1.95 microns diameter for lithium, sodium, potassium, and caesium oleates, respectively, when octane was emulsified; slightly more than twice these diameters with a heavy paraffin oil; and about half with benzol or mesitylene. (3) Bases, salts, and oleic acid greatly decrease the size of the drops. (4) The peaks of the distribution curves lie on an equilateral hyperbola. (5) The drops are about 0.060 volt negative with respect to the 0.1 molar aqueous soap solution, but this is decreased to 0.045 volt by 0.1 molar base. (6) Oleic acid inverted heptane is emulsified by sodium oleate to a water in oil emulsion.

88. Effect of humidity upon photographic speed. P. V. WELLS and J. F. HEINEKEN, E. I. du Pont de Nemours and Co., Parlin, N. J.—It is of interest in the theory of the photographic process that the speed of photographic materials depends upon their humidity during exposure. Although few quantitative data have been published it is well known that the speed is usually greater in dry atmospheres; but we have failed to find any references in the literature to the fact that with some types of photographic material the speed falls again in extremely dry atmospheres. We have investigated the humidity effect upon commercial positive and negative motion picture film. Thirty-six tests were made on cine-positives at each of the humidities 0, .20, .40, and .80, with an average deviation in a single test of less than 5 per cent in H and D speed. The effect varies with the type of film, but on the average the speed increases 7 per cent from .80 to .40 humidity, increases 7 per cent from .40 to .20 humidity, but decreases 4 per cent from .20 to 0 humidity. Twenty tests were made on four types of commercial cine-negatives at each of the above four humidities. Here again the effect varies with the type of film, but the average speed increases 7 per cent from .80 to .40 humidity, increases 9 per cent from .40 to .20 humidity, and decreases 16 per cent from .20 to 0 humidity. Most motion picture films, therefore, possess the remarkable characteristic of a maximum speed at somewhere about .20 humidity.

89. The peculiar behavior of quartz under high compression tests. S. N. PETRENKO, Bureau of Standards.—Samples of fused quartz were tested in compression, bending and tension, the elastic properties being determined with an optical extensometer. (1). *Compression test.* The compressive strength of fused quartz specimens about 0.55 in. in diameter and 2 in. long was found to depend greatly upon the medium used to distribute the pressure uniformly over the ends. The highest value, 191,000 lb/in.^{2} was obtained with a specimen having the ends covered with grease; paraffin, soft lead and paper gave much lower values. The failure was of a violent nature, the specimens disintegrating into fine powder. A modulus of elasticity of about 14,200,000 lb/in.^{2} was obtained. (2) *Transverse test.* The modulus of rupture was about 10,000 lb/in.^{2} and the modulus of elasticity about 12,000,000 lb/in.^{2}. The failure resembled that of hard steel, the specimen being always broken into three parts. (3) The results of tensile tests confirmed in general those obtained in transverse tests.

90. Projectile penetration of thin armor. L. THOMPSON and E. B. SCOTT, Naval Proving Ground, Dahlgren, Va.—Penetration data are usually compared on the basis of striking energy, and the limiting velocity (just sufficient for complete penetration) is determined by experiment in which it is attempted to secure a "straddle." The

energy absorbed by a plate is evidently a function of the velocity of impact. Results obtained with plates of one class have indicated that limiting velocities may be represented to advantage by means of the relation: $V=(psd^2/M\cos\theta)\ F(s/d,\theta)$ (V, limiting velocity, θ, angle of obliquity, s, plate thickness, d, projectile diameter, M, mass of projectile). F is a slowly varying coefficient expressing the ratio of normal momentum required to that for some definite set of values of s/d and θ. P is a specific value of normal momentum per unit volume of button punched. A number of rounds fired at thin plate with large angles of obliquity were averaged by means of this expression. Results showed unexpected co-ordination with thick plate data for small angles, in view of the tendency of thin plate to bend and dish with oblique impact.

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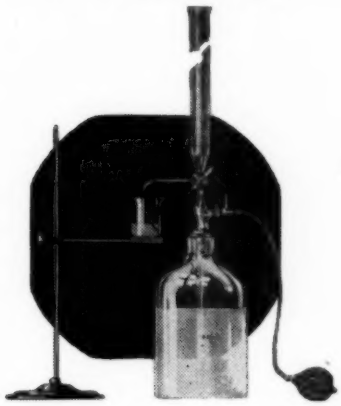

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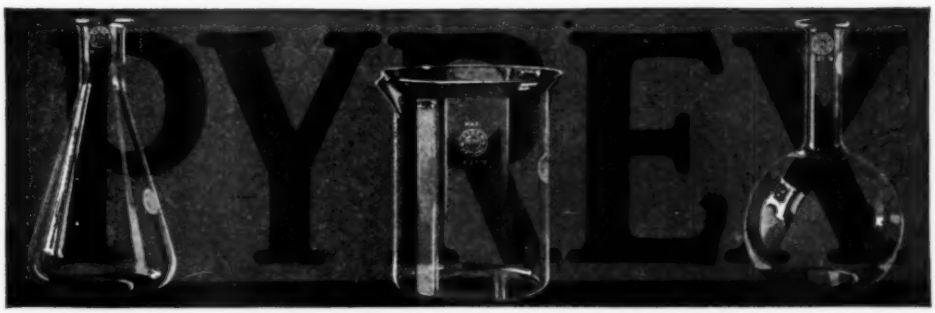

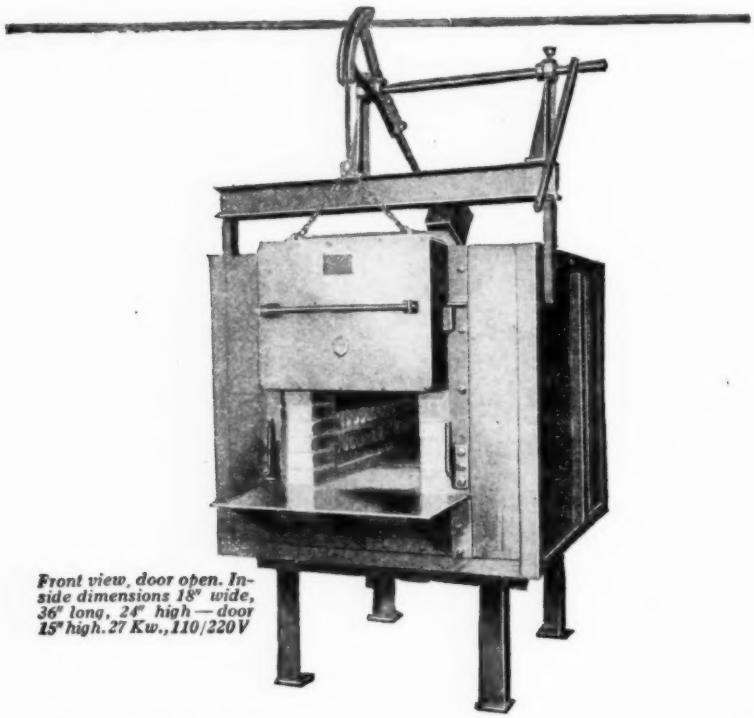

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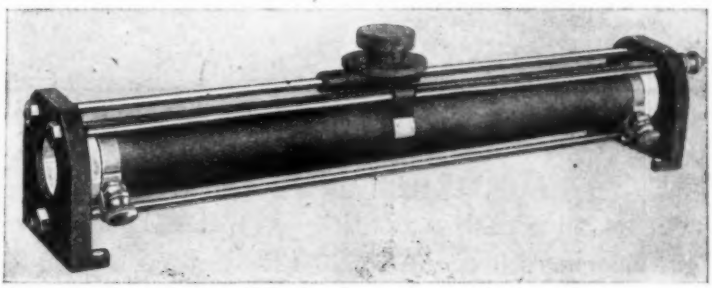

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